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ON SUBSTITUTED BENZHYDROL DERIVATIVES AND BROMCYANACETIC ETHER.[1]

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PART I.

On Substituted Benzhydrol Derivatives.

Experiments on the isomeric dibromdiphenylmethanes, $(C_6H_4Br)_2=CH_2$, were undertaken with the object of determining, if possible, the position of the two bromine atoms in the benzene rings, and the relative amounts of the different isomers produced when diphenylmethane is brominated at a low temperature. The derivatives of the general formula, $(C_6H_4Br)_2=CHX$ (in which X = Br, OH, $OCOCH_3$, etc.), were studied with especial care as these compounds are of interest because of their low points of dissociation; they lose HX at temperatures varying from 165° to 300°, and are thus found to be perfectly analogous in their reactions to benzhydrol, benzhydrol ether, diphenylmethyl bromide, and benzylic acid, whose chemistry has been so carefully worked out by Nef.[2]

[1] The work here described was performed during the years 1895-1897, under the direction of Dr. J. U. Nef, in the Kent Chemical Laboratory of the University of Chicago.

[2] Ann. Chem. (Liebig), 298, 231-256.

Paradibromdiphenylmethane, $(C_6H_4Br)_2{=}CH_2$.—The action of bromine on diphenylmethane has been studied only at high temperatures, when diphenylmethyl bromide[1] is formed. If, however, the action is carried out at low temperatures[2] and in the presence of iodine,[3] the bromine enters the benzene rings exclusively, and *p*-dibromdiphenylmethane (70 per cent) is produced together with small amounts of the corresponding *o,p*- and *o*-dibrom compounds. The exact method of work was as follows: A mixture of diphenylmethane[4] (100 grams) and iodine (10 grams—reaction goes as well with 5 grams) was cooled to 0° in a large flask which was connected with a drop-funnel and with a reflux condenser, the latter being provided with a calcium chloride tube at its upper end. By means of the drop-funnel, 200 grams of bromine (2 mols.) were added drop by drop to the contents of the flask, the latter being shaken constantly. Hydrobromic acid gas was evolved rapidly. When all the bromine had been added, the flask with its contents, which had been kept cold with ice-water, was packed in ice for twelve hours. Subsequently, the very viscous reaction-product was poured into water and the resulting highly colored, heavy oil was extracted with ether. The ethereal solution was washed with sodium hydroxide and then treated with sulphurous acid to remove the iodine, and finally dried over calcium chloride. After distilling off the ether, the residual oil was distilled in a vacuum. It practically all boiled (93 to 96 per cent yield) with slight decomposition at 246°, 47 mm. pressure; at 224°, 22 mm. pressure, or 213°, 16 mm. pressure. The thick, nearly colorless, oily distillate readily solidified in part on cooling. The semi-solid was washed at the filter-pump with cold, low-boiling ligroin, when the oily isomers, consisting of the *o,p*- and probably the *o*-dibrom compounds, dissolved, together with a considerable portion of the crystalline *p*-dibrom compound, which was found to be the chief reaction-product. By distilling off the

[1] Friedel and Balsohn: Bull. soc. chim., **33**, 339, 589; Nef: Ann. Chem. (Liebig), **298**, 232.

[2] Jackson and Field: This JOURNAL, **2**, 10.

[3] Beilstein: Ann. Chem. (Liebig), **143**, 370.

[4] Friedel and Crafts: Ann. chim. phys. [6], **1**, 478; Nef: Ann. Chem. (Liebig), **298**, 231; Radiewanski: Ber. d. chem. Ges., **27**, 3236.

ligroin from the filtrate and treating the residual oil repeatedly in the manner above described, the latter compound was largely removed from the mixture and was obtained perfectly pure by subsequent recrystallizations from low-boiling ligroin. It was not found possible at this point to separate the *p*-dibrom compound completely from its oily isomers, nor to separate the *o,p*- and the *o*-dibromdiphenylmethanes from each other, yet by the oxidation, finally, of the oily mixture to the corresponding ketones, $(C_6H_4Br)_2{=}C{=}O$, and the subsequent separation of these by crystallization, the character of the isomeric products was established (see below).

Paradibromdiphenylmethane, whose constitution as a *p*-compound was proved by its conversion into *p*-dibrombenzophenone (see below), is a white, crystalline compound. It is very soluble in ether, alcohol, benzene, glacial acetic acid, acetone, acetic ether, and carbon bisulphide. It is difficultly soluble in cold, low-boiling ligroin; hence this is the best solvent for its purification. After recrystallizing several times and subsequent drying in a vacuum over concentrated sulphuric acid, it melts sharply at 64°.

0.2025 gram substance gave 0.3568 gram CO_2 and 0.0635 gram H_2O.

0.2022 gram substance gave, by the Carius method, 0.2320 gram AgBr.

	Calculated for $(C_6H_4Br)_2{=}CH_2$.	Found.
C	47.85	48.04
H	3.06	3.48
Br	49.07	49.08

Paradibromdiphenylmethyl Bromide, $(C_6H_4Br)_2{=}CHBr$.—This compound was obtained by treating *p*-dibromdiphenylmethane with bromine at 150°.[1] The process was carried out with an apparatus similar to the one already described for the preparation of dibromdiphenylmethane. To *p*-dibromdiphenylmethane, heated to 150°, bromine (slightly more than 1 mol.) was added drop by drop, the containing flask being constantly shaken. Hydrobromic acid gas was evolved vigor-

[1] Friedel and Balsohn: Bull. soc. chim., 33, 339.

ously, and when all the bromine had been added the reaction was practically over. When cold, the light-brown, crystalline mass was broken up and water was added. The crystals were filtered off, thoroughly washed with water, dried, and then purified by recrystallizing from ether, or from ligroin, or from a mixture of the two.

It should be noted here that the mother-liquors left from the purification of *p*-dibromdiphenylmethyl bromide invariably gave off hydrobromic acid gas, no matter how carefully the ether or ligroin solution had been freed previously from this acid. The mother-liquors also always deposited crystals of *p*-dibrombenzophenone, $(C_6H_4Br)_2{=}C{=}O$ (m. p. 172° to 173°). These crystals, which are long, flat, and thin (sometimes in plates), with obliquely cut ends, possess a pearly luster, and can thus readily be detected among the fine, needle-like crystals of *p*-dibromdiphenylmethyl bromide. They can also be distinguished from the bromide crystals by the fact that they give no reaction with concentrated sulphuric acid, while the latter give a deep-red color with this reagent.

Paradibromdiphenylmethyl bromide is a white, crystalline compound, very soluble in alcohol (by which it is slowly decomposed), benzene, and chloroform; less soluble in ether and ligroin. Hence, the two latter solvents are best used for its purification. It melts at 106° to 107°.

0.2275 gram substance gave 0.3250 gram CO_2 and 0.0538 gram H_2O.

0.1940 gram substance gave, by the Carius method, 0.2680 gram AgBr.

	Calculated for $(C_6H_4Br)_2{=}CHBr$.	Found.
C	38.52	38.96
H	2.22	2.62
Br	59.25	59.09

Paradibromdiphenylmethyl bromide, as well as the corresponding benzhydrol derivatives, gives a deep-red color with concentrated sulphuric acid.[1] It cannot be distilled even under diminished pressure because of its very low point of dissociation. On heating the compound to 165° in absence of

[1] Nef: Ann. Chem. (Liebig), 298, 241.

air, hydrobromic acid escapes and *p*-tetrabromtetraphenylethylene, $(C_6H_4Br)_2=C=C=(C_6H_4Br)_2$, is formed. When heated above its melting-point in a stream of dry air, it is largely oxidized to *p*-dibrombenzophenone, $(C_6H_4Br)_2=C=O$. If treated with water under proper conditions, *p*-dibrombenzhydrol ether, $(C_6H_4Br)_2=CH-O-CH=(C_6H_4Br)_2$, is produced. Treatment with sodium acetate leads to the formation of *p*-dibrombenzhydrol acetate,

$$(C_6H_4Br)_2=CH-O-CO-CH_3,$$

while with sodium ethylate or with ethyl alcohol, *p*-dibrombenzhydrol ethyl ether,

$$(C_6H_4Br)_2=CH-O-C_2H_5,$$

results. All these reactions are self-evident from the standpoint of a methylene dissociation.[1]

Two attempts to isolate *p*-dibromdiphenylmethylene bromide, $(C_6H_4Br)_2=CBr_2$, through treating *p*-dibromdiphenylmethyl bromide with bromine (1 mol.) at 150°, were unsuccessful. On treating the reaction-product with water, *p*-dibrombenzophenone (m. p. 172° to 173°) was obtained quantitatively. Friedel and Balsohn[2] report that they were unable to purify the corresponding diphenylmethane dibromide, $(C_6H_5)_2=CBr_2$, and state that it gave benzophenone when heated to 150° with water. Apparently, *p*-dibromdiphenylmethylene bromide is so unstable that when it is merely brought into contact with water it is decomposed in an analogous manner.

Paradibrombenzophenone, $(C_6H_4Br)_2=CO$.—This compound was repeatedly produced in small quantities as a side-product in the experiments on *p*-dibromdiphenylmethane and its derivatives. A carbon and hydrogen analysis of this ketone was carried out when it was obtained as a decomposition-product through heating *p*-dibrombenzhydrol (see below), and it was analyzed for bromine when it was formed as a decomposition-product through heating *p*-dibrombenzhydrol

[1] Nef: *Ibid.*, **298**, 231–241.

[2] Bull. soc. chim., **33**, 337–339.

ethyl ether (see below). The results of these analyses are here given :

0.2047 gram substance gave 0.3441 gram CO_2 and 0.0450 gram H_2O.

0.2690 gram substance gave, by the Carius method, 0.2967 gram AgBr.

	Calculated for $(C_6H_4Br)_2=CO$.	Found.
C	45.88	45.84
H	2.33	2.44
Br	47.05	47.18

This ketone was obtained quantitatively by oxidation of *p*-dibrombenzhydrol, $(C_6H_4Br)_2=CHOH$, by means of chromic acid. To a weighed quantity of this alcohol (see below) dissolved in glacial acetic acid, the calculated quantity of finely powdered potassium bichromate was added gradually, and the mixture heated for some time. The oxidation was known to be complete when a drop of the solution no longer gave a red color with concentrated sulphuric acid. On addition of water, a crystalline compound was precipitated, which, when filtered, washed, dried, and recrystallized from ligroin, showed the characteristic, slender, flat crystals which have been described above. It melted at 172° to 173°, and it gave no red color with concentrated sulphuric acid. This ketone was likewise quantitatively produced by oxidizing *p*-dibromdiphenylmethane in glacial acetic acid solution with chromic acid.

That the compound produced in all these reactions is *p*-dibrombenzophenone, is proved by its identity with *p*-dibrombenzophenone which has been prepared in other ways by E. Hofmann,[1] by Schöpf,[2] and by Cathcart.[3] The compound obtained in the present case was, furthermore, converted into the oxime (following Schäfer's[4] method for the preparation of *p*-monobrombenzophenone oxime), and a compound melting at 150° to 152° was obtained.[5] This oxime, when crystallized

[1] Ann. Chem. (Liebig), **264**, 162.
[2] Ber. d. chem. Ges., **24**, 3767.
[3] *Ibid.*, **25**, 3302.
[4] Ann. Chem. (Liebig), **264**, 154.
[5] Cathcart: Ber. d. chem. Ges., **25**, 3302.

from ligroin, appeared in two distinct forms, each melting sharply at 150° to 152°. One modification consisted of long, slender, needle-like crystals[1] and the other of flat, rhombic ones. When the latter were redissolved in ligroin and the solution "seeded" with the needle-like crystals, all of the compound was obtained in the form of needles, with the melting-point 150° to 152°. These two crystalline forms of this oxime have not been previously mentioned.

When *p*-dibrombenzophenone was reduced in acid solution, some *p*-dibrombenzhydrol (m. p. 115° to 116°) was obtained, and also a crystalline compound (m. p. 158° to 161°), which may have been the corresponding pinacone,[2] was isolated, but this was not further investigated.

Orthoparadibrombenzophenone, $(C_6H_4Br)_2{=}CO$.—The isomeric dibromdiphenylmethanes obtained by brominating diphenylmethane at a low temperature, consist, as stated above, of about 70 per cent of the crystalline *p*-dibrom compound; about 27 per cent is the *o*,*p*-compound, while the remainder is probably the *o*-dibrom derivative. This was proved as follows: A mixture of 150 grams of the oily dibromdiphenylmethanes, from which the *p*-compound had been removed as completely as possible in the manner already described, was transformed successively in a manner analogous to that described for the conversion of *p*-dibromdiphenylmethane into the corresponding bromides, $(C_6H_4Br)_2{=}CHBr$, then into the acetates, $(C_6H_4Br)_2{=}CH{-}O{-}CO{-}CH_3$, and into the alcohols, $(C_6H_4Br)_2{=}CH{-}OH$. As none of these compounds could be obtained in a crystalline condition, the alcohols were finally oxidized to the corresponding ketones by means of chromic acid in glacial acetic acid solution. Thus, a mixture of 90 grams of oily ketones was obtained from which 7 grams of *p*-dibrombenzophenone (m. p. 170° to 172°) separated out on cooling. These oily ketones boiled smoothly at 226° and 14 mm. pressure; under considerable decomposition at 323°, ordinary pressure. After some weeks' standing in a cool place, a crystalline compound (60 grams) was deposited

[1] Hofmann: Ann. Chem. (Liebig), **264**, 164.
[2] Linnemann: *Ibid.*, **133**, 27.

slowly and was separated by filtration. This compound, when recrystallized from low-boiling ligroin, appeared in groups of large, flat crystals having squarely cut ends, and melted at 50° to 52°. That this body is identical with *o*,*p*-dibrombenzophenone obtained by Heidenreich[1] from *o*-brombenzoyl chloride and brombenzene in presence of aluminium chloride, was proved by converting a portion of it into its oxime (m. p. 140° to 142°); this oxime was thereupon converted into the corresponding indoxazene compound, which crystallizes in white needles (m. p. 132° to 133°). These transformations were carried out according to Heidenreich's method. The melting-points and other properties of the compounds produced correspond to those given by this investigator.

A bromine determination of the *p*-bromphenyl indoxazene obtained gave the following figures:

0.1538 gram substance gave, by the Carius method, 0.1053 gram AgBr.

	Calculated for $C_{13}H_8BrNO$.	Found.
Br	29.19	29.25

An attempt was made to obtain *o*,*p*-dibrombenzhydrol by reducing *o*,*p*-dibrombenzophenone with sodium amalgam. The experiment was carried out as in the reduction of the *p*-dibrom ketone, but instead of obtaining the *o*,*p*-dibrombenzhydrol sought, a partial elimination of the bromine was effected. Through a quantitative examination of the solution in which the reduction had been carried out, it was proved that 11 per cent of the bromine had been removed from the weight of *o*,*p*-dibrombenzophenone used.

It seemed probable that the oil from which the *o*,*p*-dibrombenzophenone crystals had been separated must be the corresponding *o*-dibrom ketone. But when an attempt was made to form its oxime, a crystalline compound (2.7 grams out of a possible 5.3 grams) which melted at 140° to 141° was obtained. This body, when heated with sodium ethylate in a sealed tube, gave an indoxazene which melted at 128° to 129°.

[1] Ber. d. chem. Ges., 27, 1453.

As these melting-points correspond so closely with those of *o,p*-dibrombenzophenone oxime and of *p*-bromphenyl indoxazene, respectively, it must be inferred that at least 50 per cent of the oil consisted of *o,p*-dibrombenzophenone.

Paratetrabromtetraphenylethylene, $(C_6H_4Br)_2{=}C{=}C{=}(C_6H_4Br)_2$.—It has been stated already that when *p*-dibromdiphenylmethyl bromide is heated hydrobromic acid escapes, and if no air is present *p*-tetrabromtetraphenylethylene is formed quantitatively, as follows:

$$2(C_6H_4Br)_2 : CHBr \rightarrow 2(C_6H_4Br)_2 : C \rightleftarrows + 2HBr \rightarrow (C_6H_4Br)_2 : C : C : (C_6H_4Br)_2 + 2HBr.$$

If, however, air is present, the methylene derivative may be partially or entirely oxidized to the ketone:

$$(C_6H_4Br)_2 : CHBr + O \rightarrow (C_6H_4Br)_2 : C \rightleftarrows + O + HBr \rightarrow (C_6H_4Br)_2 : C : O + HBr.$$

Thus, when a stream of dry air was drawn through molten *p*-dibromdiphenylmethyl bromide, not more than half the resulting product consisted of the polymerized ethylene derivative, while the remainder was *p*-dibrombenzophenone (m. p. 172° to 173°). This explains why solutions containing *p*-dibromdiphenylmethyl bromide oxidize spontaneously on standing at the ordinary temperature, with loss of hydrobromic acid, to the corresponding *p*-dibrombenzophenone.

It was found that *p*-tetrabromtetraphenylethylene was formed most smoothly when *p*-dibromdiphenylmethyl bromide was heated in a distilling-bulb so arranged that a stream of dry air was drawn through the neck and arm of the bulb, but not through the molten bromide. Under these conditions, the bromide begins to lose hydrobromic acid gas as soon as the temperature of the bath reaches 165°. The temperature was finally raised to 230°–240° and kept there for some hours. The resulting deeply colored residue was dissolved in benzene and thoroughly digested with animal charcoal. Finally the benzene was distilled off and the residue dissolved in hot alcohol; on cooling, tiny, white, needle-like crystals separated out. The presence of any *p*-dibrombenzophenone was

readily detected by examination of the first crystals which appeared, and this body was removed mechanically if found. The ethylene derivative, after several recrystallizations from glacial acetic acid, and careful drying for some days in a vacuum over fused caustic potash, melted sharply at 248°.

0.2378 gram substance gave 0.4174 gram CO_2 and 0.0559 gram H_2O.

	Calculated for $(C_6H_4Br)_2=C=C=(C_6H_4Br)_2$.	Found.
C	48.14	47.87
H	2.47	2.61

A molecular weight determination by the freezing-point method, using benzene as a solvent, gave the following results:

	I.	II.
Weight of benzene	30 grams	30 grams
" " compound	0.2110 grams	0.3810 grams
Depression of freezing-point	0°.055	0°.110
Molecular weight found	638.1	577.3
" " calculated for $(C_6H_4Br)_2 : C : C : (C_6H_4Br)_2$		648

An attempt to form the corresponding ethane derivative through reduction of this ethylene compound by means of zinc and acetic acid was unsuccessful. The original ethylene compound (m. p. 248°) was entirely recovered. This compound also refuses to take up bromine.

Paratetrabromtetraphenylethylene is possibly also one of the decomposition-products of *p*-dibrombenzhydrol through heat (see below).

Paradibrombenzhydrol Acetate, $(C_6H_4Br)_2=CH—O—CO—CH_3$. — When *p*-dibromdiphenylmethyl bromide is treated with sodium acetate (1.5 mols.) in glacial acetic acid solution, the corresponding *p*-dibrombenzhydrol acetate is formed.[1] Five such experiments with quantities of the bromide varying from 5 grams to 23 grams were carried out, and in each case nearly quantitative yields were obtained by heating only a few minutes on an asbestos plate under a reflux condenser in order to complete the reaction.

[1] Friedel and Balsohn: Bull. soc. chim., 33, 338; Vincent: *Ibid.*, 35, 304.

On addition of water, an oil separated out, which was extracted with ether, washed with an alkali, and dried over calcium chloride. The ether was distilled off and the oily residue was dissolved in hot ligroin; on cooling, very short, fine, needle-like crystals, which melted at 70° to 72°, were obtained. The compound burned with some difficulty but a carbon and hydrogen analysis gave the following results:

0.2077 gram substance gave 0.3532 gram CO_2 and 0.0645 gram H_2O.

	Calculated for $(C_6H_4Br)_2=CH-O-CO-CH_3$.	Found.
C	46.87	46.38
H	3.12	3.44

Paradibrombenzhydrol acetate is very soluble in most organic solvents, but less so in low-boiling ligroin. With concentrated sulphuric acid, it gives the characteristic deep-red color given by the bromide under similar conditions. When heated with water or with alcoholic potash it gives *p*-dibrombenzhydrol.

Paradibrombenzhydrol, $(C_6H_4Br)=CHOH$.—This compound was best prepared by the action of alcoholic potash (1.5 mols.) upon *p*-dibrombenzhydrol acetate. The reaction was completed in the cold after standing a few hours, or on heating, in a few minutes. A small amount of *p*-dibrombenzophenone usually crystallized out from this alcoholic solution and was separated by filtration. The alcoholic filtrate, when poured into water, gave a fine, white, crystalline precipitate of *p*-dibrombenzhydrol, which was purified by recrystallizing from a mixture of ether and ligroin. Very long, fine, white needles, melting at 115° to 116°, were obtained.

0.2007 gram substance gave 0.3335 gram CO_2 and 0.0574 gram H_2O.

	Calculated for $(C_6H_4Br)_2=CHOH$.	Found.
C	45.61	45.32
H	2.92	3.17

Paradibrombenzhydrol was also obtained by the action of water in slightly diluted acetic acid solution upon *p*-dibrombenzhydrol acetate.

Paradibrombenzhydrol is very soluble in ether, alcohol, and acetic acid, but very little soluble in ligroin. When ground in an agate mortar, it shows remarkable electric properties. With concentrated sulphuric acid it gives the characteristic deep-red color already mentioned. When treated with ethyl alcohol in presence of concentrated sulphuric acid, *p*-dibrombenzhydrol ethyl ether is formed, while with benzene in presence of the same acid, *p*-dibromtriphenylmethane results. Both of these compounds will be described below. With oxidizing agents, *p*-dibrombenzophenone is produced.

Paratetrabromtetraphenylethane, $(C_6H_4Br)_2{=}CH{-}CH{=}(C_6H_4Br)_2$.—The behavior of benzhydrol at its dissociation-point (300°) has been thoroughly investigated by Nef.[1] The following experiments show that when *p*-dibrombenzhydrol is heated to its dissociation-point (162°), analogous reactions take place, except that in one case a fair amount of *p*-tetrabromtetraphenylethylene was also obtained.

a. Paradibrombenzhydrol (4 grams), when heated in a distilling-bulb in a metal-bath, began to give off water at 162°. The temperature of the bath was gradually raised to 250°, when the reaction was complete. The fused mass, on heating to 300° for five minutes longer, grew dark in color, therefore the operation was discontinued. The mass was digested with hot benzene, which left a portion insoluble in ether, alcohol, glacial acetic acid, carbon bisulphide, acetic ether, acetone, chloroform, carbon tetrachloride, but soluble in hot nitrobenzene. On recrystallizing from this solvent, a compound (1.5 grams), which melted above 300° and which gave no color-reaction with concentrated sulphuric acid, was obtained. An analysis proved this body to be *p*-tetrabromtetraphenylethane.

0.1961 gram substance gave 0.3442 gram CO_2 and 0.0531 gram H_2O.

0.1938 gram substance gave, by the Carius method, 0.2224 gram AgBr.

[1] Ann. Chem. (Liebig), 298, 241.

	Calculated for $(C_6H_4Br)_2=CH-CH=(C_6H_4Br)_2$.	Found.
C	48.00	47.87
H	2.77	3.00
Br	49.23	49.09

On examination, the benzene solution, decolorized by digesting with animal charcoal, was found to contain a crystalline compound little soluble in alcohol, from which it was recrystallized till pure. Glistening, flat, slender crystals (0.9 gram), which melted at 172° to 173°, were obtained. This compound, through its properties and analysis (see above), was proved to be *p*-dibrombenzophenone.

The mother-liquors left from recrystallizing *p*-dibrombenzophenone were found to contain a small amount of a crystalline compound melting at 85°—probably a mixture of *p*-dibromdiphenylmethane and *p*-dibrombenzophenone.

b. Paradibrombenzhydrol (2 grams) was placed in a distilling-bulb connected with a U-tube, and a stream of dry air was drawn through the apparatus, while the metal-bath was heated quickly to 250° and kept there for five minutes. Water condensed in the delivery-tube and in the U-tube. The white, crystalline residue was extracted with ether. After adding ligroin and distilling off the ether, hexagonal, transparent crystals of *p*-dibrombenzhydrol ether (see below), melting at 150° to 152°, were deposited.

c. Paradibrombenzhydrol (5 grams) was heated for forty minutes (bath at 300°) in a distilling-bulb provided with a thermometer, and so arranged that a distillate and any evolved gas could be collected. Water distilled off, but no gas was obtained. The crystalline residue was completely dissolved in hot benzene. On distilling off this benzene and redissolving in alcohol, the following compounds were separated by fractional crystallization: *p*-Dibrombenzophenone (1.5 grams) melting at 172° to 173°, *p*-dibromdiphenylmethane (0.4 gram) melting at 63° to 64°, and a compound (0.4 gram) melting at 252° to 254°, which, from its small, needle-like crystals, its solubilities and its melting-point (though this was slightly higher than that given above for the pure substance), was thought to be *p*-tetrabromtetraphenylethylene.

d. In a small flask through which a stream of dry carbon dioxide was constantly drawn and which was arranged under a reflux condenser, *p*-dibrombenzhydrol (5 grams) was heated to 300° for eight hours. The resulting crystalline residue was nearly all dissolved in hot alcohol, and from this solution the following compounds were separated by fractional crystallization: *p*-Dibrombenzophenone (0.6 gram) melting at 172° to 173°, a trace of the body described under *c*, melting at 250° to 254°, also mixtures melting from 120° to 170°, from 170° to 230°, from 160° to 164°. The small residue insoluble in alcohol, left in the bulb, melted at 275°, but there was not a sufficient amount for further purification. It is probable that *p*-dibrombenzophenone, *p*-dibrombenzhydrol ether, possibly *p*-tetrabromtetraphenylethylene, and the corresponding ethane derivative were present in these mixtures, but this was not proved.

Paradibrombenzhydrol Ether, $(C_6H_4Br)_2{=}CH{-}O{-}CH{=}(C_6H_4Br)_2$.—The experiments just described prove that when *p*-dibrombenzhydrol is heated, *p*-dibrombenzhydrol ether is first formed, but since this ether has a dissociation-point only very slightly higher than its alcohol, it cannot, therefore, be isolated in quantity by this process. The best method for the preparation of this compound is to heat *p*-dibromdiphenylmethyl bromide with water.[1] Five grams of the bromide with 20 cc. of water and the amount of calcium carbonate necessary to destroy the hydrobromic acid formed, were heated in a sealed tube at 120° for twenty hours. The residue, which was insoluble in water, was recrystallized from low-boiling ligroin. Two compounds crystallized out, and these were separated mechanically. One (3.35 grams) consisted of masses of short crystals radiating from a center and melting at 148° to 150°; the other (0.2 gram consisted of the long, slender, flat crystals of *p*-dibrombenzophenone, melting at 172 to 173°. On recrystallizing the main reaction-product from ligroin, and finally from alcohol, it melted at 155° to 156°.

[1] Nef: Ann. Chem. (Liebig), 298, 232.

0.2248 gram substance gave 0.3834 gram CO_2 and 0.0577 gram H_2O.

0.2152 gram substance gave, by the Carius method, 0.2426 gram AgBr.

	Calculated for $(C_6H_4Br)_2=CH—O—CH=(C_6H_4Br)_2$.	Found.
C	46.84	46.51
H	2.70	2.85
Br	48.04	48.18

Paradibrombenzhydrol ether is extremely soluble in benzene and in chloroform; less so in alcohol, ether, and ligroin. It gives a deep-red color with concentrated sulphuric acid. That it is not acted upon by boiling with alcohol was proved by heating it (1 gram) with alcohol (15 cc.) in a sealed tube at 100° for thirty hours. The compound was entirely recovered unchanged. On the other hand, heating with acetic acid, very readily converts it, as well as the corresponding *p*-dibrombenzhydrol, into *p*-dibrombenzhydrol acetate—a fact which, in view of the low point of dissociation of both this ether and its alcohol, is easily understood.

Paradibrombenzhydrol Ethyl Ether, $(C_6H_4Br)_2=CH—O—C_2H_5$.—This compound was formed by allowing an alcoholic solution of *p*-dibromdiphenylmethyl bromide to stand in the cold; but the bromide, in the presence of a molecular quantity of cold alcoholic sodium ethylate reacted almost instantly. To insure complete reaction, the mixture was heated a short time; on pouring it into water, an oil separated out which was extracted with ether. This was well washed and then dried over calcium chloride. After distilling off the ether, the residual oil, when distilled in a stream of carbon dioxide, boiled at 228° at 16 mm. pressure. All attempts to distil this oil in presence of air, even under diminished pressure, resulted in the formation of some *p*-dibrombenzophenone.

0.2642 gram substance gave 0.4685 gram CO_2 and 0.0967 gram H_2O.

0.3650 gram substance gave, by the Carius method, 0.3692 gram AgBr.

	Calculated for $(C_6H_4Br)_2=CH-O-C_2H_5$.	Found.
C	48.64	48.36
H	3.78	4.06
Br	43.24	43.25

Paradibrombenzhydrol ethyl ether is a thick, colorless oil with a characteristic, not unpleasant, odor. With concentrated sulphuric acid it gives a deep-red color.

That *p*-dibrombenzhydrol ethyl ether can also be obtained from *p*-dibrombenzhydrol or its corresponding ether, by means of ethyl alcohol and concentrated sulphuric acid, was proved by experiment. This reaction is self-evident, in view of the experiments of Linnemann[1] and Nef,[2] and in view of the low dissociation-point of these substances.

Behavior of p-Dibrombenzhydrol Ethyl Ether on Heating.—Paradibrombenzhydrol ethyl ether has a low dissociation-point. It breaks down at 300° into ethyl alcohol, ethylene (?), *p*-dibrombenzophenone, and *p*-dibromdiphenylmethane. The ether (6.5 grams), placed in a small distilling-bulb which was connected with a second distilling-bulb (receiver) and an azotometer, was heated in a metal-bath to 300° for three hours, when the reaction was complete. A small amount of liquid (b. p. 110°) distilled into the receiver, and at the same time 120 cc. of gas were collected in the azotometer. This gas, which burned with a smoky flame, was probably ethylene. The distillate separated into two layers, one, a a thin liquid, which, when redistilled, came over between 65° to 78° and gave the iodoform test, and was, therefore, probably ethyl alcohol; the other, an oil which had a wintergreen odor and which completely decomposed when an attempt was made to redistil it. The highly-colored crystalline residue left in the distilling-bulb was dissolved entirely in benzene and the solution was decolorized by digesting with animal charcoal. After distilling off the benzene, the residue was dissolved in alcohol. From this solution *p*-dibrombenzophenone (2 grams), melting at 172° to 173°, and *p*-dibromdiphenylmethane (0.6 gram), melting at 62° to 64°, were sepa-

[1] Ann. Chem. (Liebig), 133, 17.
[2] *Ibid.*, 298, 255.

rated by fractional distillation; the melting-points are those obtained after recrystallizing from low-boiling ligroin.

The result of a bromine determination of the *p*-dibrombenzophenone here obtained has been given above.

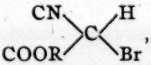
Paradibromtriphenylmethane, $(C_6H_4Br)_2{=}CH{-}C_6H_5$. — Paradibrombenzhydrol, treated with benzene and concentrated sulphuric acid, gives *p*-dibromtriphenylmethane.[1] A solution of *p*-dibrombenzhydrol (3 grams) in benzene (50 cc.) was treated with concentrated sulphuric acid (15 cc.). After standing twelve hours in the cold, the highly-colored benzene solution was decanted from the acid, well washed, and then dried over calcium chloride. On distilling off the benzene, a thick oil with a yellowish-green fluorescence was left. It solidified at the end of ten days. The compound distilled without decomposition at 260°, 15 mm. pressure., but still showed a yellowish-green fluorescence. It was found to be remarkably soluble in all organic solvents, but was finally purified by dissolving in alcohol and digesting repeatedly with animal charcoal. The alcoholic solution gave, on adding water, nearly a gram of a compound crystallizing in very fine, almost white, needles, and melting sharply at 100°.

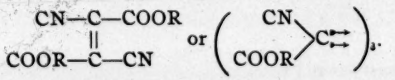
0.2141 gram substance gave 0.4426 gram CO_2 and 0.0687 gram H_2O.

0.1980 gram substance gave, by the Carius method, 0.1850 gram AgBr.

	Calculated for $(C_6H_4Br)_2{=}CH{-}C_6H_5$.	Found.
C	56.71	56.38
H	3.48	3.56
Br	39.80	39.94

PART II.

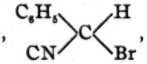
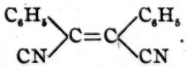
On Bromcyanacetic Ether,  , *and Its Conversion by Loss of Hydrobromic Acid into Dimolecular or Trimolecular Cyanmethylenecarboxylic Ether*,



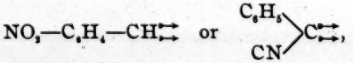
The main results of this work on bromcyanacetic ether have

[1] Nef: Ann. Chem. (Liebig), 298, 254.

already been tabulated briefly by Nef.[1] It has since been sharply proved by him[2] that all primary and secondary alkyl haloids react with various reagents because they are partially dissociated, *i. e.*, alkylidene and HX particles are present, and the speed of the reaction[3] of alkyl haloids depends solely upon the number of such dissociated particles present at a given temperature. Thus, *p*-dibromdiphenylmethyl bromide, whose dissociation-point lies at about 165°, reacts instantly with alcoholic sodium ethylate, or slowly with alcohol, in the cold, whereas ethyl iodide, dissociation-point about 450°, reacts very slowly with alcoholic sodium ethylate in the cold and not at all with alcohol alone at 100°. At 150°, however, ethyl ether is formed.

There are some substituted alkyl haloids, however, as pointed out by Nef,[4] which show a very peculiar behavior when treated with alcoholic sodium ethylate or other so-called double decomposition reagents. Thus, *o*- and *p*-nitrobenzyl chloride give, in marked contrast to benzyl chloride, by treatment with alcoholic potash (or sodium ethylate) no trace of an ether, $NO_2—C_6H_4—CH_2—O—C_2H_5$ (or only small amounts),[5] but quantitative or relatively large amounts of the stilbene derivatives, *o*- and *p*-$NO_2—C_6H_4—CH=CH—C_6H_4—NO_2$. Brombenzyl cyanide,  , gives, on similar treatment, dicyanstilbene,  .

These results can only be understood, as pointed out by Nef, on the basis that the methylene residues, which become free when HX is removed by the alkali,



[1] Ann. Chem. (Liebig), **298**, 258.

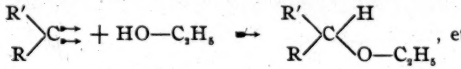
[2] *Ibid.*, **309**, 126; **318**, 316.

[3] In this way I believe the percentage of dissociation at various temperatures may be determined as accurately as the percentage of ionization of electrolytes by the conductivity method. J. U. Nef.

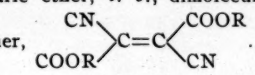
[4] Ann. Chem. (Liebig), **298**, 229, 257–260.

[5] Thiele: *Ibid.*, **305**, 103.

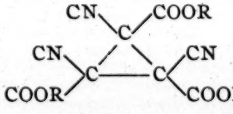
in these cases unite, in part or entirely, with each other to give the olefine derivatives mentioned above; whereas, ordinarily, the alkylidene residues absorb the reagent (alcohol, etc.) set free, or present as such, to give an addition-product,



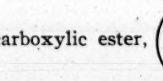
Bromcyanacetic ether is another such compound. It gives, as will be seen from what follows, on treatment with sodium, aniline, the sodium salts of malonic ether, and of cyan- and acetoacetic ether, a large amount (up to 67 per cent) of a crystalline compound (m. p. 120° to 122°), which, in view of the facts tabulated above, would naturally be regarded as dicyanfumaric ether, *i. e.*, dimolecular cyanmethylenecarboxylic ether,



In 1900, Errara and Perciabosco[1] published a paper on the action of halogens on sodium cyanacetic ether. They found that this ether is converted by iodine, or bromine, into a crystalline compound melting at 119°, and they also obtained the same compound through the action of sodium cyanacetic ether upon bromcyanacetic ether. The compound is obviously identical with that mentioned above and obtained in various ways, as indicated, from bromcyanacetic ether. These observers consider that the compound under discussion is tricyantrimethylenetricarboxylic ether,



, *i. e.*, trimolecular cyanmethylenecarboxylic ester,

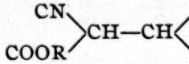


, and this is very probable because of its conversion by saponification and subsequent loss of carbon dioxide[2] into known trimethylene tri- and tetracarboxylic acids. They also give

[1] Ber. d. chem. Ges., **33**, 2978.

[2] Scacherl: Ann. Chem. (Liebig), **229**, 89; Büchner: *Ibid.*, **284**, 197.

molecular weight determinations confirming this conclusion—which, however, are to be regarded as uncertain[1] (see below).

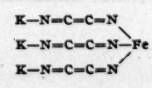
Finally, it should be mentioned that Thorpe and Young[2] have recently obtained a crystalline substance, melting at 120°, from sodium cyanacetic ether and iodine, to which they give the formula  . This is obviously identical with the dimolecular or trimolecular cyanmethylenecarboxylic ester under discussion. The analytical data given by Thorpe and Young must therefore be erroneous.

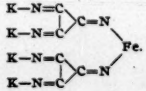
Preparation of Bromcyanacetic Ether.—This compound was prepared by adding bromine (1 mol.) slowly to cyanacetic ether which was heated in a bath at 150°, care being taken to avoid access of moisture. The crude reaction-product was distilled directly under reduced pressure. A 60 to 75 per cent yield was obtained.

Bromcyanacetic ether is a colorless oil with a somewhat piercing odor, boiling at 110° to 112°, at 18 mm. pressure, and between 195° to 200° at ordinary pressure, but with considerable decomposition. Treated with aqueous iodide of potassium, iodine is at once set free in the cold—a reaction frequently used as a test for this compound.

0.3348 gram substance gave 0.3839 gram CO_2 and 0.0940 gram H_2O.

[1] Should further investigations, which I intend to make in the near future, confirm the formula of Errara and Perciabosco, it should be emphasized that this is one of the few instances yet known in which a methylene derivative polymerizes to a trimolecular modification (cf. polymeric fulminic acid, Ann. Chem. (Liebig), 280 316). Azulmic acid, $(CNH)_x$, the polymerized isocyanides, $(RNC)_x$, the polymeric phenyl- and diphenylmethylenes, $(C_6H_5CH)_x$, $[(C_6H_5)_2C]_x$, are unquestionably all very complex polymers. Finally, I have on the basis of my bivalent carbon work for the past eight years, given in my lectures (cf. also Ann. Chem. (Liebig), 298, 215, 313) the following very probable formulas to potassium ferri- and ferrocyanide, respectively:





J. U. Nef.

[2] J. Chem. Soc. (London), 77, 937.

0.3228 gram substance gave 21 cc. N at 18° and 743.7 mm. pressure.

0.1976 gram substance gave, by the Carius method, 0.1923 gram AgBr.

	Calculated for $C_5H_6NO_2Br$.	Found.
C	31.25	31.26
H	3.12	3.11
N	7.29	7.39
Br	41.66	41.41

Conversion of Bromcyanacetic Ether into Di- or Tri-molecular Cyanmethylenecarboxylic Ester.

a. By Means of Sodium.—Bromcyanacetic ether in benzene (or ethereal) solution reacted at once in the cold when treated with sodium (1 or 2 mols.) in the form of fine wire. On digesting the salt residue with hot benzene the benzene filtrates gave, on concentration and cooling, a 60 per cent yield of polymeric cyanmethylenecarboxylic ether, melting at 120° to 124°.

0.2193 gram substance gave 0.4325 gram CO_2 and 0.0905 gram H_2O.

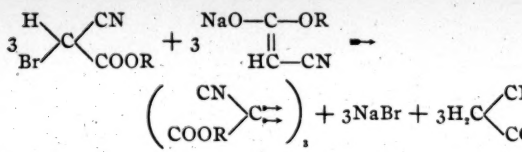
0.2058 gram substance gave 0.4024 gram CO_2 and 0.0871 gram H_2O.

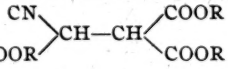
0.2008 gram substance gave 22.5 cc. N at 17° and 747.5 mm. pressure.

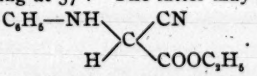
	Calculated for $\left(\begin{smallmatrix}CN\\COOR\end{smallmatrix}\!\!>\!C\!\!<\right)_x$	Found. I.	Found. II.
C	54.05	53.78	53.32
H	4.50	4.58	4.70
N	12.61	12.82	....

b. By Means of Sodium Cyanacetic Ether.—Five grams of sodium cyanacetic ether, suspended in absolute ether, were slowly treated in the cold with an ethereal solution of 7.1 grams (1 mol.) of bromcyanacetic ether and the mixture finally heated for four hours under a reflux condenser. Three and two-tenths grams of cyanacetic ether (80 per cent of the theory) boiling at 204°, and 2.7 grams of cyanmethylenecar-

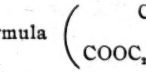
boxylic ether (67 per cent yield), melting at 120° to 122°, were obtained as reaction-products:



c. By Means of Sodium Acetoacetic Ether and of Sodium Malonic Ether.—These reactions were not carried out quantitatively and therefore need repetition. The operations took place in absolute ethereal solutions and were accomplished, especially in the latter case, with considerable evolution of heat. In the first case the formation of much free acetoacetic ether, as well as of polymeric cyanmethylenecarboxylic ester (40 per cent yield), melting at 120° to 122°, was unquestionably established. In the latter case, some of the polymeric methylene derivative (7 per cent) melting at 120° was isolated. Besides this a small amount of a crystalline compound, volatile with steam and melting at 45° to 47°, which may possibly be  was obtained.

d. By Means of Aniline.—Bromcyanacetic ether and aniline (1.5 mols.), in ethereal solution, reacted on each other in the cold. After standing forty-eight hours, a yield of 25 per cent of the theoretical amount of polymerized cyanmethylenecarboxylic ester (119° to 120°) was obtained. The other products formed, besides phenylammonium bromide, were a substance with odor of bromcyanogen, and a crystalline compound melting at 57°. The latter may possibly be the anilido derivative,  .

Properties of Di- or Trimolecular Cyanmethylenecarboxylic Ester.—The crystalline substance formed in all the reactions discussed above melts, when thoroughly purified by crystallizing from benzene, at 122°. It is very sparingly soluble in

cold ether and ligroin, and quite soluble in chloroform and hot benzene. Acetone, acetic ether, and especially hot alcohol, dissolve it freely, but gradually act upon it. The molecular weight determinations by the freezing-point method in benzene, given by Errara and Perciabosco,[1] agree with the trimolecular formula  (theory = 333).

These determinations were repeated with the following results, which agree better with the dimolecular formula (222), and which prove that Errara and Perciabosco worked in one case with a supersaturated solution:

	I.	II.
Weight of substance	0.0963 gram	0.1381 gram
" " benzene	17.4313 "	26.5160 "
Depression of freezing-point	0°.120	0°.116
Molecular weight found	225	220

	III.	IV.
Weight of substance	0.2550 gram	0.3586 gram
" " benzene	26.5160 "	30.6115 "
Depression of freezing-point	0°.182	0°.180
Molecular weight found	258	317

Determinations I. and II. only are reliable, since solutions III. and IV. were proved to be supersaturated as follows: Solution III. was cooled to its freezing-point and maintained at this temperature (as indicated by a Beckmann thermometer) for ten minutes. Thereupon, 10 cc. of the supernatant liquid were transferred to a weighed dish and the following results obtained by evaporation to dryness. Volume of solution = 10 cc.; sp. gr. of benzene at 5° = 0.8885; weight of benzene used = 8.885 grams; weight of solid residue = 0.0826 gram. From these data it is clear that 0.0092 gram of substance dissolve in 1 gram of benzene at 5°. In one of the molecular weight determinations given by Errara and Perciabosco, 0.01157 gram of substance to 1 gram of benzene were used, therefore the solution in this case was supersaturated. In the other molecular weight determination given by them an exactly saturated solution was used.

[1] Ber. d. chem. Ges., 33, 2981.

In view of these data, molecular weight determinations were carried out by the boiling-point method, using McCoy's apparatus,[1] and the following very curious results were obtained:

	I.	II.
Weight of substance	0.5088 gram	0.6042 gram
Volume of benzene	18 cc.	24.1 cc.
Elevation of boiling-point	0°.210	0°.190
Molecular weight found	441	443
	III.	IV.
Weight of substance	0.6042 gram	0.5676 gram
Volume of benzene	26 cc.	23.7 cc.
Elevation of boiling-point	0°.155	0°.161
Molecular weight found	491	490

The only experimental evidence, therefore, which exists at present in favor of Errara and Perciabosco's trimolecular formula is the conversion of the compound by saponification and subsequent loss of carbon dioxide into known trimethylene derivatives as mentioned above.

In conclusion, the writer wishes to express her most grateful appreciation to Dr. Nef for his kindness, for his numerous suggestions, and for the unvarying patience and constant interest with which he followed the progress of this work.

Contribution from the New York Agricultural Experiment Station.

THE STATUS OF PHOSPHORUS IN CERTAIN FOOD MATERIALS AND ANIMAL BY-PRODUCTS, WITH SPECIAL REFERENCE TO THE PRESENCE OF INORGANIC FORMS.

By E. B. Hart and W. H. Andrews.

The following research forms part of and is preliminary to an extended investigation to be carried on at this station under the direction of Dr. W. H. Jordan on the metabolism of phosphorus and sulphur in the animal body.

It is quite generally believed that phosphorus exists in plant substances, partly in organic combinations as nucleo-

[1] This Journal, **23**, 353.

proteids, nucleins and lecithins, and partly in inorganic forms, such as calcium, magnesium,[1] and potassium phosphates. It is not difficult to understand how this view of the occurrence of phosphorus in vegetable tissue originated, since inorganic combinations form the basis of supply to the growing plant and since it is in the ash that we have chiefly studied the kinds and proportions of the inorganic plant constituents. Starting with the assumption that a considerable proportion of the phosphorus in animal and human vegetable foods is inorganic in form, our efforts have been directed towards the elaboration of a method for separating and quantitatively estimating, at least approximately, this form of phosphorus in vegetable and animal feeding-stuffs.

It was also thought that should the ratio of organic to inorganic phosphorus vary greatly in the different vegetable products, this fact might be made the basis of investigations as to the relative nutritive value of these products for specific purposes.

Such investigations could be undertaken, however, only after the evolution of a fairly safe method for the separation of inorganic from organic phosphorus.

Total Phosphorus.

Before taking up the experimental details of the estimates of inorganic phosphorus, determinations of total phosphorus were made on a number of vegetable and animal products by both the magnesium nitrate and the Neumann methods. The Neumann method was tried particularly because it is convenient for use on large volumes of liquids, a condition which must be met in the separations involved in this inquiry.

Magnesium Nitrate Method.—This method is essentially the same as that used by the Association of Official Agricultural Chemists:[2] Five grams of material were well mixed in a platinum dish with 2 to 4 cc. of a solution of magnesium nitrate and incinerated at a low heat. In most cases a perfectly white ash was obtained. This residue was dissolved in dilute

[1] Sherman: U. S. Dept. Agr., Bull. 121.

[2] Bull. 46, Revised Edition, Bureau Chem., Dept. of Agr.

hydrochloric acid, made up to 200 cc., an aliquot being taken for the estimation of total phosphorous.

Neumann Method.—This is the method described by Neumann[1] and already used by Sherman:[2] Five grams of material were placed in a Kjeldahl flask, 10 to 15 cc. concentrated sulphuric acid were added, and the mixture was heated over a low flame until well charred. When partly cooled, 5 to 10 grams of ammonium nitrate were added and the digestion continued. Further additions of ammonium nitrate were made from time to time to entirely oxidize and decolorize the mixture. On cooling, the residue was rinsed into a 200 cc. flask, diluted to the mark, and an aliquot was taken for the determination of total phosphorus by the molybdate-magnesium method. The large amount of ammonium sulphate formed on neutralizing with ammonia seems to impede the precipitation of ammonium phosphomolybdate and only when a generous excess of ammonium molybdate was added—150 cc.—did we get a rapid separation of the yellow precipitate.

Table I.

Substance.	Percentage of phosphorus found in air-dry material. Magnesium nitrate method.	Neumann method.
Corn	0.313	0.310
Oats	0.355	0.339
Wheat bran	1.548	1.537
Malt sprouts	0.677	0.670
Brewer's grains	0.421	0.419
Distiller's grains	0.307	0.303
Linseed meal	0.789	0.787
Oat straw	0.135	0.129
Alfalfa	0.266	0.267
Meat meal	4.073	3.971
Liver meal	1.034	1.029
Dried blood	0.123	0.126
Cow feces	0.344	0.353

The two methods yield practically the same results.

Separation of Organic and Inorganic Phosphorus.

Iwanow[3] has lately studied the changes occurring in the

[1] Dubois Reymond's Archiv. (Physiol. Abth.), 1897, pp. 552–553.
[2] J. Am. Chem. Soc., 24, 1105 (1902).
[3] Ber. d. bot. Ges., 20, Heft 7 (1902).

organic phosphorus combinations during the germination of vetch (*Vicia sativa*) and has reached the conclusion that there is a gradual decrease of organic phosphorus with corresponding increase of the inorganic forms as germination proceeds. The seeds were germinated in the dark. The method of separation used by Iwanow was as follows: Five to seven grams of the material were warmed on the water-bath ten to fifteen minutes with 100 to 150 cc. of 1 per cent acetic acid. After cooling, the precipitated proteid matter was separated by filtration through a small flannel filter and washed with water until about 500 cc. filtrate had been collected. For the determination of the inorganic phosphorus, an aliquot from the 500 cc. was taken and precipitated directly with molybdate solution.

Zaleski,[1] working independently and on the same problem, evolved an almost identical method. This investigator recommends the use of either a 1 per cent acetic acid or 0.2 per cent hydrochloric acid solution as the extracting reagent. As will be shown later in both of these methods, the cleavage action on soluble nucleins of the nitric acid contained in the molybdate solution is not sufficiently taken into account. It is true that Zaleski recommends that no extra nitric acid be added, he himself using only the ordinary molybdate solution.

Kossel,[2] working on muscle extracts, has used a mixture of tannin and 5 per cent hydrochloric acid as the precipitant of proteids containing phosphorus.

Araki[3] has recently used this method, somewhat modified, in his studies of the decomposition of nucleic acids by enzymes. The method of Araki is as follows: Two grams of a salt of nucleic acid were dissolved in 40 cc. of water and to this the enzyme was added. This solution was then diluted with an equal volume of water, 4 grams of sodium acetate added, and tannin so long as a precipitate continued to be formed. The filtrate from this precipitate, according to Araki, should contain any free phosphoric acid split off by the

[1] *Ibid.*, **20**, Heft 7 (1902).
[2] Ztschr. physiol. Chem., **7**, 9 (1883).
[3] *Ibid.*, **38**, 84 (1903).

action of the enzyme. In our hands, as we shall show later, tannic acid in dilute mineral acid solution and tannic acid with sodium acetate both fail to completely precipitate the soluble nucleins contained in certain of our feeding-materials. We do not assume to deny the accuracy of the results of these authors, recognizing the important fact that the constitution and consequent reaction of the nucleic acids with which these investigators worked may be entirely different from those that occurred in our materials.

Our preliminary work was done on whole oats, ground and air-dried. Five-gram samples were treated with 125 cc. of the extracting reagent for varying lengths of time, with occasional vigorous shakings. The mixtures were then allowed to settle and the supernatant liquid was decanted through dry filters into 500 cc. flasks. The residue was washed by decantation with several portions of water until 500 cc. of filtrate had been collected. To 200 cc. of this filtrate 10 grams of ammonium nitrate were first added, and after heating the solution to 65° C., 50 cc. of ordinary ammonium molybdate solution were added, the whole kept at 65° C. for fifteen minutes, then removed from the bath and allowed to stand for one hour. The precipitate was then filtered off, washed with a small quantity of water, and the phosphorus estimated as magnesium pyrophosphate. This was supposed to be the inorganic phosphorus. The total soluble phosphorus was determined in another aliquot of 200 cc. by the Neumann method. The phosphorus in the insoluble residue, representing a mixture of nucleoproteids, nucleins, and lecithins, was also determined and designated as insoluble organic phosphorus. Tannin, with acetic and hydrochloric acids, under the conditions shown in the table on the following page, was also tried. The molybdate solution used was one prepared according to the method adopted by the Official Agricultural Chemists.[1]

These results show how decided a variation may occur in the quantities of the different forms of phosphorus as estimated under varying conditions of manipulation. They also

[1] Bull. 46, Revised Edition, Bureau Chem. Dept. of Agr.

Table II.

Substance.	Acid.	Total phosphorus.	Percentage of phosphorus in air-dry material.			
			Insoluble organic phosphorus.	Soluble phosphorus.	Inorganic phosphorus.	
Oats		0.355	0.210	0.142	0.035	
1	1 per cent acetic, 12 mm., 55° C.		0.240	0.116	0.042	
1	" room temp., 24 hours		0.227	0.138	0.032	
1	" " 40 "		0.252	0.103	0.017	
1	" " 3 "		0.258	0.092	0.006	
0.2	" hydrochloric, room temp., 40 hours		0.184	0.171	0.014	
0.5	" " 10 mm., 55° C.		0.094	0.244		
1	" acetic, room temp., 17 hours, tannin		0.206	0.126		Tannin interferes.
0.2	" hydrochloric, room temp., 17 hours, tannin		0.075	0.240		
1	" acetic, 10 mm., 55° C., tannin		0.223	0.109		
0.2	" hydrochloric, 10 mm., 55° C., tannin					

show in certain instances an apparent inorganic content appreciably large, while in others practically none was found, indicating again the influence of certain varying factors in the method of separation. That tannin fails to remove a large proportion of soluble organic forms is also very evident.

We next made the same separations with a number of materials, using, as the extracting reagents, 0.2 per cent hydrochloric and 1 per cent acetic acid solutions for forty hours at room temperature. The inorganic phosphorus was estimated by the same method as that used in the case of oats.

Table III.

Substance.	Acid.	Total phosphorus.	Percentage of phosphorus in air-dry material.		
			Insoluble organic phosphorus.	Soluble phosphorus.	Inorganic phosphorus.
Wheat bran	Acetic	1.548	0.111	1.422	1.230
	Hydrochloric		0.428	1.121	0.120
Malt sprouts	Acetic	0.677	0.176	0.479	0.389
	Hydrochloric		0.213	0.477	0.350
Brewer's grains	Acetic	0.421	0.382	0.042	0.005
	Hydrochloric		0.395	0.032	0.006
Distiller's grains	Acetic	0.307	0.229	0.082	0.022
	Hydrochloric		0.244	0.075	0.022
Corn	Acetic	0.313	0.155	0.163	0.017
	Hydrochloric		0.159	0.153	0.015
Alfalfa	Acetic	0.266	0.057	0.205	0.174
	Hydrochloric		0.084	0.189	0.136
Linseed meal	Acetic	0.789	0.470	0.327	0.166
	Hydrochloric		0.564	0.195	0.102
Liver meat meal	Acetic	1.034	0.488	0.618	0.347
	Hydrochloric		0.486	0.585	0.380
Dried blood	Acetic	0.123	0.099	0.020	0.019
	Hydrochloric		0.080	0.042	0.045
Cow feces	Acetic	0.344	0.193	0.159	0.091
	Hydrochloric		0.199	0.141	0.084

It will be noticed from these results that whenever there is a large amount of total soluble phosphorus there is also a

corresponding increase in the amount of inorganic phosphorus. In but one instance—that of the hydrochloric acid extract of bran—did this fail to hold true. In all cases, the character of the inorganic precipitate was greatly different from that of an ammonium phosphomolybdate precipitate. It was invariably of a flocculent, proteid-like nature, and only on standing did the characteristic yellow precipitate begin to separate. This certainly indicated a slow cleavage of the organic phosphorus in the solution which was brought about by the excess of nitric acid in the molybdate reagent. In the case of the acetic acid extract from bran, this cleavage was especially marked. Such conditions of manipulation certainly lead to results altogether too high for inorganic phosphorus.

To determine more definitely the point as to whether certain nucleic acids are so easily split up as our results indicated, we made preparations of these bodies from wheat bran and fresh corn-germ meal. That from wheat bran was separated by Osborn's method[1] and gave a product extremely low in phosphorus, less than 1 per cent, and high in proteid matter. The filtrate from the pepsin digestion—a part of the Osborne method—showed an abundance of an easily cleavable organic phosphorus combination. This is in harmony with our other results, that the nucleins or salts of nucleic acid of wheat bran are extremely soluble in dilute acid solutions.

By Levene's method[2] we separated from wheat bran a nucleic acid carrying 7.59 per cent of phosphorus, and from fresh germ meal one containing 6.83 per cent. Both these products were soluble in water, yielding pale-yellow solutions. When dissolved in water and tested as in the above method for the estimation of inorganic phosphorus, that is, with 50 cc. molybdic solution at 65° C. in the presence of ammonium nitrate, a flocculent precipitate first separates. This soon takes on a yellow color and the ammonium phosphomolybdate settles out.

It became apparent that a method estimating, at least ap-

[1] Ann. Rep. Conn. Agr. Exp. Sta., 1901.
[2] J. Am. Chem. Soc., **22**, 239 (1900).

proximately, the amount of inorganic phosphorus in our feeding materials and animal by-products, must take into account the amount of free acid in the precipitating reagent. With this point in view, we first established the amount of nitric acid necessary to separate quantitatively ammonium phosphomolybdate when neutral ammonium molybdate was added to a neutral solution of inorganic phosphorus. We found that 2 cc. of nitric acid of sp. gr. 1.20 in 225 cc. of solution would cause quantitative separation in water extracts and in extracts made with 0.2 per cent hydrochloric acid and neutralized with ammonia. In the 1 per cent acetic acid extracts, neutralized with ammonia, 4 cc. of nitric acid of sp. gr. 1.20 are necessary because of the retarding action of the ammonium acetate on the separation of ammonium phosphomolybdate. Ten grams of ammonium nitrate were added to the above volume. Neutral ammonium molybdate was prepared by addition of ammonia to the ordinary molybdate solution, using litmus as an indicator.

Preliminary estimations showed that forty hours' extraction was entirely unnecessary. Three hours, the time required to thoroughly wash the residue, gave nearly as high total soluble phosphorus as forty hours. In the next table is presented results secured by the following method: Five grams of the sample were vigorously shaken with 125 cc. of the extracting reagent for 15 minutes. The mixture was then allowed to settle, was decanted through a filter-paper into a 500 cc. flask, and the residue washed with water until about 500 cc. of filtrate had been collected. Two hundred cc. of the filtrate were next neutralized with ammonia, using litmus as indicator, and 10 grams of ammonium nitrate added. The solution was then warmed to 65° C. and, in the case of the water and hydrochloric acid extracts, 2 cc. nitric acid (sp. gr. 1.20) and 25 cc. neutral ammonium molybdate were added. To the acetic acid extracts 4 cc. nitric acid (sp. gr. 1.20) were added. The extracts were allowed to stand fifteen minutes at 65°, were then removed from the bath and after one hour were filtered. The phosphorus was estimated as the magnesium salt.

Table IV.

Substance.	Treatment.	Percentage of phosphorus in air-dry material. Total phosphorus.	Total soluble phosphorus.	Inorganic phosphorus.
Oats	Water	0.355	0.180	0.00
	Acetic		0.114	0.00
	Hydrochloric		0.096	0.00
Bran (wheat)	Water	1.548	0.356	0.143
	Acetic		1.100	0.055
	Hydrochloric		0.951	0.036
Malt sprouts	Water	0.677	0.548	0.391
	Acetic		0.489	0.279
	Hydrochloric		0.477	0.017
Brewer's grains	Water	0.421	0.142	0.007
	Acetic		0.039	0.007
	Hydrochloric		0.040	0.009
Distiller's grains	Water	0.307	0.079	0.012
	Acetic		0.104	0.005
	Hydrochloric		0.069	0.007
Corn	Water	0.313	0.276	0.014
	Acetic		0.203	0.00
	Hydrochloric		0.177	0.00
Alfalfa	Water	0.266	0.196	0.064
	Acetic		0.182	0.079
	Hydrochloric		0.180	0.079
Linseed meal	Acetic	0.789	0.327	0.085
	Hydrochloric		0.195	0.088
Oat straw	Acetic	0.135	0.095	0.028
	Hydrochloric		0.086	0.009
Wheat	Water	0.390	0.125	0.028
	Acetic		0.174	0.040
	Hydrochloric		0.172	0.008
Blood	Water	0.123	0.029	0.005
	Acetic		0.028	0.010
	Hydrochloric		0.054	0.00
Meat meal	"	4.073	1.387	0.098
Liver meat meal	"	1.034	0.486	0.005
Cow feces	"	0.344	0.148	0.004

These results clearly show that where the amount of nitric acid used in the determination of inorganic phosphorus was reduced to the minimum, there was a marked decrease in the amount of this form of phosphorus apparently present. This decrease is especially noticeable in the hydrochloric acid ex-

tracts. In fact the estimations by the use of hydrochloric acid, with the exceptions of alfalfa and linseed meal, we regard as indicating the absence of inorganic phosphates. The water and acetic acid extracts of bran and malt sprouts show considerably higher figures for inorganic phosphorus than the hydrochloric acid extract. It will be observed that both these materials are rich in easily soluble, organic compounds. That these compounds are more easily split up into inorganic forms by water alone and 1 per cent acetic acid than by 0.2 per cent hydrochloric acid seems a possible explanation of the results secured. Even when bran has been extracted with a 1 per cent solution of hydrochloric acid for forty hours, the inorganic estimation showed but 0.088 per cent, while the total soluble phosphorus was 1.26 per cent. We found it impossible to filter extracts of linseed meal and, consequently, could only prepare such extracts by decantation. This, of course, gave us a distintly turbid solution. On precipitating with molybdate solution, an unusually large, flocculent precipitate resulted, difficult to filter and wash. It redissolved readily in ammonia. Also in the case of alfalfa, a very large, flocculent precipitate was formed on adding the molybdate solution. Later, working with sprouted grains, we estimated in one case as inorganic phosphorus 0.0118 gram magnesium pyrophosphate. This precipitate, after ignition, was unusually white. On dissolving it in dilute nitric acid and reestimating the phosphorus, we weighed but 0.0017 gram of magnesium pyrophosphate. This is an extreme case, but it indicated that where we have a large, flocculent, proteid precipitate with our molybic acid, soluble again in ammonia, there can be formed on the addition of magnesia mixture insoluble proteid-magnesia combinations convertible to magnesium oxide on ignition and weighed as magnesium pyrophosphate. With this precaution in mind, we redetermined the inorganic phosphorus in alfalfa and linseed meal. On the first weighing as magnesium pyrophosphate they showed respectively 0.0072 and 0.0107 gram. On dissolving in dilute nitric acid, we weighed as magnesium pyrophosphate 0.0006 gram and 0.0005 gram, respectively. These figures are equiva-

lent to 0.008 per cent inorganic phosphorus in alfalfa and 0.007 per cent in linseed meal, figures we still believe due to errors of manipulation.

Experiments with the Use of Tannin and Sodium Acetate.

Since Araki has used this method as a means of separating nucleic acids from solutions containing organic and inorganic phosphorus, it was thought that it might be applied to our work. Extracts were made with 0.2 per cent hydrochloric and 1 per cent acetic acids in the usual way. To 200 cc. of the extract, neutralized with ammonia, 12 grams of sodium acetate were added and then a solution of tannin until no further precipitate was formed. The mixture was then diluted to 250 cc., filtered through a dry filter, and in 200 cc. the total phosphorus (supposedly inorganic) determined by the Neumann method. The reagents used were phosphorus free.

Table V.

Substance.		Percentage of phosphorus in air-dry material. Total phosphorus.	Inorganic phosphorus.
Wheat	Water	0.390	0.087
	Acetic		0.147
	Hydrochloric		0.147
Bran	Water	1.548	0.398
	Acetic		1.026
	Hydrochloric		0.783
Distiller's grains	Water	0.307	0.080
	Acetic		0.092
	Hydrochloric		0.063
Malt sprouts	Water	0.677	0.528
	Acetic		0.471
	Hydrochloric		0.483
Brewer's grains	Water	0.421	0.115
	Acetic		0.061
	Hydrochloric		0.026
Oat straw	Water	0.135	0.094
	Acetic		0.061
	Hydrochloric		0.083

These results give further evidence that tannin and sodium acetate could not be used for the separation of organic and inorganic phosphorus in such materials.

Method Adopted.

The method we have finally adopted as giving results nearest the truth is that detailed above for the hydrochloric acid extract of Table IV., with the following modification: After ignition the magnesium pyrophosphate is dissolved in dilute nitric acid and the phosphorus reestimated. This, as detailed above, is to prevent the error of weighing magnesium pyrophosphate contaminated with magnesium oxide. We do not expect the method to give absolute results in all cases. What we claim for it is that it reduces the hydrolyzing action of the reagents to a minimum, but at the same time allows complete precipitation of inorganic phosphates.

In one experiment, when to a solution containing 0.0413 gram of inorganic phosphorus estimated as magnesium pyrophosphate, were added 0.500 gram of nucleic acid prepared from wheat bran, and the solution then subjected to the above treatment, the recovery was 0.0439 gram, a gain of 0.0026 gram by cleavage of the nucleic acid present. This 0.0026 gram of magnesium pyrophosphate calculated in percentage of phosphorus on a 2 gram sample is equal to 0.036 per cent. It can be readily seen, then, that estimations of inorganic phosphorus giving results as high as 0.036 per cent in solutions rich in soluble organic phosphorus can easily be accounted for as coming by cleavage of organic phosphorus compounds.

Attempts have been made to remove the interfering proteids by precipitation with neutral ammonium molybdate in solutions cooled to 18° C. and in the presence of but 1 cc. nitric acid (sp. gr. 1.20) in 250 cc. volume. This did bring about partial removal, but on warming the solutions with the addition of the extra 1 cc. of nitric acid (sp. gr. 1.20), necessary to precipitate the inorganic phosphorus, there was generally a further precipitation of proteid matter and consequent interference.

Experiments with Germinated Grains.

Since Iwanow[1] and Zaleski,[2] working independently, have

[1] Ber. d. bot. Ges., 20, Heft. 7 (1902).
[2] *Ibid.*, 20, Heft. 7 (1902).

shown that during the germination in the dark of vetch and lupine, a marked decrease in organic phosphorus with corresponding increase in inorganic forms appeared to take place, it became of interest to carry on similar work, using our own method for the separation of inorganic phosphorus. Both these workers used the ordinary molybdate solution containing free nitric acid in their inorganic determinations. For our work we selected corn, oats, and wheat. These were germinated in pure glass sand in the dark for periods of one and two weeks. At the ends of these periods, the grains were dried at 60° C., separated from the adhering sand, and finely ground. After exposure to the air for a few days the samples were bottled and analysis made by the hydrochloric acid method. Below we give the data, and for comparison, results obtained on the unground seeds. We also present data secured on the two-weeks-old germinated seeds by the Iwanow method. Fifty cc. of ordinary molybdate were used to 200 cc. of extract. Iwanow does not state the exact quantity of molybdic solution which he used, so we are unable to exactly repeat his method.

Table VI.

Substance.	Treatment.	Total phosphorus.	Percentage of phosphorus in air-dry material.		
			Total soluble phosphorus.	Inorganic phosphorus.	Iwanow method. Inorganic phosphorus.
Wheat	Ungerminated	0.390	0.172	0.008	
	1 week		0.211	0.018	
	2 weeks		0.279	0.031	0.273
Corn	Ungerminated	0.313	0.177	0.00	
	1 week		0.237	0.011	
	2 weeks		0.312	0.036	0.212
Oats	Ungerminated	0.355	0.096	0.00	
	1 week		0.181	0.022	
	2 weeks		0.302	0.032	0.217

We see from the above figures that during the germination of these seeds in the dark there is a marked increase in solu-

ble organic phosphorus compounds, but that according to our method of estimation the cleavage does not extend to the formation of inorganic phosphates. The increase of inorganic phosphorus accompanying the increase of total soluble organic phosphorus is explained by the slight cleavage action of our reagents.

The Iwanow[1] method in our hands gives results in perfect agreement with his previously reported results—that is, that during germination in the dark there is a marked formation of inorganic phosphorus.

The discrepancy in the two results appears to be due to differences of method. Araki,[2] working on the action of certain enzymes, as pepsin, trypsin, and crepsin, and on nucleic acids of animal origin, came to the conclusion that the structure of these bodies was but little disturbed by the action of these enzymes.

Our results bring us to the conclusion that during germination there is a proteolysis of nucleoproteids with formation of more soluble mobile nucleins and nucleic acids, but not a transformation of the organic phosphorus into the inorganic.

Summary.

(1) Our commercial feeding-stuffs of vegetable origin do not contain appreciable quantities of phosphorus in inorganic combination.

(2) The animal feeding-materials, such as liver meal and dried blood, when representative, are also approximately free from this form of phosphorus. Commercial meat meal, liable to carry varying quantities of bone, does contain inorganic phosphorus, dependent, of course, on the amount of bone present. The feces of the cow used in our experiment are also free from inorganic phosphorus.

(3) Germinated grains are rich in forms of soluble organic phosphorus.

(4) Germination, extending over a period of two weeks, on oats, corn, and wheat, did not transform organic phosphorus into inorganic forms.

[1] *Loc. cit.*

[2] Ztschr. physiol. Chem., 38, 84 (1903).

In conclusion, we wish to express to Dr. Jordan, at whose instigation this work was undertaken as preliminary to studies on phosphorus and sulphur metabolism in animals, and to Dr. Van Slyke, our sincere thanks for their constant interest and many helpful suggestions.

THE CHLORIDES OF PARABROMORTHOSULPHOBENZOIC ACID AND SOME OF THEIR DERIVATIVES.[1]

By William M. Blanchard.

PART I.

The interesting results obtained in the study of the chlorides of orthosulphobenzoic acid[2] and the chlorides of paranitroorthosulphobenzoic acid[3] led to an investigation of the chlorides of parabromorthosulphobenzoic acid. The work was undertaken by Edward S. Smith at the suggestion of Professor Remsen. Smith prepared a large quantity of pure acid potassium salt of parabromorthosulphobenzoic acid from which he obtained the mixed chlorides. By treating a portion of the mixed chlorides with ammonia he isolated the symmetrical chloride, and by fractional crystallization of another portion, he obtained several crystals of the unsymmetrical chloride in pure condition.

At this point Smith left the university, and it was with the material that he had prepared, and at Professor Remsen's suggestion, that the present author took up the work.

Soon after the work was begun, greater interest was given to it by the appearance of an article by List and Stein,[4] in which it was stated that several of the conclusions in the papers already referred to were erroneous, that the two chlorides furnish an interesting case of tautomerism, that each individual chloride reacts at one time as a symmetrical, and at

[1] From the author's dissertation submitted, June, 1900, to the Board of University Studies of the Johns Hopkins University, in conformity with the requirements for the degree of Doctor of Philosophy.

[2] This Journal, 17, 330, 347; 18, 794, 809, 819.

[3] *Ibid.*, 19, 496.

[4] Ber. d. chem. Ges., 31, 1648.

another time as an unsymmetrical compound, and that it is not possible to determine with certainty the constitution of either chloride by means of chemical investigation.

The experimental part of this work will now be presented, after which some remarks will be made upon the conclusions to be drawn therefrom.

Acid Potassium Salt of Parabromorthosulphobenzoic Acid.— The material that formed the basis of this work was parabromtoluene. This was obtained in crystalline form, melting at about 32° to an almost colorless liquid. It was sulphonated and oxidized by a method differing but slightly from that described by Hübner and Post.[1] To the parabromtoluene in a large flask fuming sulphuric acid was added in the proportion of 5 parts by weight of acid to 2 parts by weight of bromtoluene, the acid being added in small portions and the temperature kept down to about 40°, by placing the flask in cold water when necessary. The reaction was complete in an hour. The clear, dark-brown solution was poured into about ten times its volume of cold water, the excess of sulphuric acid neutralized with calcium carbonate, and the precipitated calcium sulphate removed by filtration. The filtrate was heated to boiling, a slight excess of potassium carbonate added, and the boiling continued for at least an hour to insure the complete conversion into the carbonate of all the magnesium, which is usually found to some extent in commercial calcium carbonate. When this precaution was not observed, it was found extremely difficult to separate and purify the salt desired. The precipitated calcium and magnesium carbonates were filtered off and the filtrate evaporated to a smaller volume, when, on cooling, a large quantity of crystals was obtained. By fractional crystallization, these were separated into two salts, potassium parabrommetatoluenesulphonate crystallizing in needles, and the corresponding ortho salt crystallizing in plates or thin, lustrous scales. The latter is similar n appearance to the sodium parabromorthotoluenesulphonate described by Hübner and Post, and identical with the potas-

[1] Ann. Chem. (Liebig), 169, 1.

sium salt prepared by Remsen and de Roode[1] by another method.

The potassium salt was then oxidized as follows: Into a 5-liter balloon flask containing about 4 liters of water, 90 grams of the salt, to be separately oxidized, were introduced. The flask was placed on an asbestos plate over a burner and connected with a boiler from which a current of steam was passed into the solution of the salt. After the solution had begun to boil, 100 grams of powdered potassium permanganate were added in small quantities at short intervals. The boiling was continued for twelve hours, when the oxidation was complete. During the operation the flame beneath the flask and the current of steam passing into the solution were so regulated that the quantity of water in the flask remained almost constant. When the salt was all oxidized, the excess of potassium permanganate was reduced with alcohol, the manganese dioxide allowed to settle, and the solution removed by decantation, and afterwards filtered. This was evaporated to a small volume and allowed to cool, when sufficient concentrated hydrochloric acid was added to precipitate the difficultly soluble acid potassium salt of parabromorthosulphobenzoic acid. This salt crystallizes from its aqueous solution in large, lustrous plates, and is identical with that prepared by Remsen and Bayley:[2]

	Calculated for $C_6H_3Br\langle^{COOH}_{SO_2OK}$	Found.
K	12.22	12.15

Symmetrical Chloride.—The symmetrical chloride was prepared by the method employed for the preparation of the symmetrical chloride of orthosulphobenzoic acid. A mixture of powdered acid potassium salt of parabromorthosulphobenzoic acid and phosphorus pentachloride, in the proportion of 70 grams of the former to 114 grams of the latter, was placed in an evaporating dish on a water-bath and heated for an hour, the whole being frequently stirred during the heating.

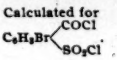
[1] This JOURNAL, 13, 222.
[2] *Ibid.*, 8, 230.

At the end of an hour the reaction was complete. The oily product was poured into a large beaker of cold water, where it soon solidified to a slightly yellowish, crystalline mass. This was powdered, washed with cold water, and dried. It was then treated with a cold solution of ammonia, made by adding 1 part of concentrated aqueous ammonia to 3 parts of water, until a portion crystallized from purified ligroin (boiling at 105° to 140°) showed a definite melting-point. The whole was then crystallized from the ligroin, which had been purified by the usual method. The symmetrical chloride melts at 99° to 100°.

The determinations of chlorine in the chloride were made by the method employed by Saunders.[1] Portions of the chloride were decomposed in beakers by warming with concentrated nitric acid, to which silver nitrate had been added:

I. 0.1908 gram substance gave 0.1716 gram AgCl.[2]

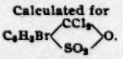
II. 0.2369 gram substance gave 0.2124 gram AgCl.

	Calculated for 	Found. I.	II.
Cl	22.30	22.24	22.17

Unsymmetrical Chloride.—The unsymmetrical chloride was prepared by the method devised by List and Stein[3] for the preparation of the unsymmetrical chloride of orthosulphobenzoic acid. The neutral potassium salt of parabromorthosulphobenzoic acid was heated with phosphorus oxychloride in a sealed tube at 130° for fifteen hours. For every 50 grams of the neutral salt, 75 grams of the phosphorus oxychloride were used. The yield was something over 50 per cent. When crystallized from ligroin, the unsymmetrical chloride melts at 89° to 90°.

I. 0.1542 gram substance gave 0.1393 gram AgCl.[4]

II. 0.2238 gram substance gave 0.2011 gram AgCl.

	Calculated for 	Found. I.	II.
Cl	22.30	22.34	22.22

[1] This JOURNAL, 17, 350.

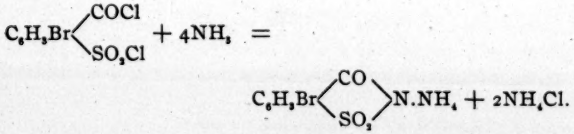
[2] Analysis made by E. S. Smith.

[3] *Loc. cit.*

[4] Analysis made by E. S. Smith.

Ammonia on the Symmetrical Chloride.—To 50 cc. concentrated, aqueous ammonia 5 grams finely powdered symmetrical chloride were added. The chloride was completely dissolved in about an hour. The solution was allowed to stand in the open air until the excess of ammonia had evaporated. The vessel was then found to contain a quantity of long, interlacing, needle-like crystals. When these were dissolved in water and sufficient hydrochloric acid added, a voluminous precipitate came down, which, when collected and crystallized from water, was found to be parabrombenzoic sulphinide, prepared first by Remsen and Bayley,[1] and later by Remsen and De Roode.[2] The filtrate from the parabrombenzoic sulphinide was evaporated to a smaller volume and examined for parabromorthocyanbenzenesulphonic acid. The addition of potassium carbonate gave no precipitate, and closer examination failed to reveal the presence of either the potassium or the ammonium salt of this acid.

This experiment was repeated a number of times, the conditions being varied, but always with the same result, whether the solution of ammonia was concentrated or dilute, cold or hot; the product was only parabrombenzoic sulphinide. It was found that the symmetrical chloride dissolves in cold, concentrated, aqueous ammonia in about an hour, while it is not completely dissolved in a solution made by mixing 1 part of concentrated ammonia with 1 part of water, before the end of four days. When the dilute ammonia is warmed, however, the chloride goes into solution in the course of a few hours:



Ammonia on the Unsymmetrical Chloride.—To a concentrated solution of aqueous ammonia 5 grams of the unsymmetri-

[1] This JOURNAL, 8, 229.
[2] *Ibid.*, 13, 230.

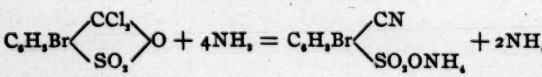
cal chloride were added. The chloride dissolved immediately, giving rise to a marked evolution of heat. After the excess of ammonia had evaporated, the solution was acidified with hydrochloric acid. The addition of the acid gave a white precipitate, which proved to be brombenzoic sulphinide, described above. The filtrate from the sulphinide was evaporated to a smaller volume, when the addition of potassium carbonate gave a precipitate of potassium parabromorthocyanbenzenesulphonate.[1]

This experiment was repeated several times, under different conditions, and always with the same result. Both brombenzoic sulphinide and parabromorthocyanbenzenesulphonic acid were formed. Several experiments were performed in order to determine the relative amounts of the two products under different conditions. In each experiment 5 grams of the chloride were taken. The results are tabulated in grams.

	I.	II.	III.
1. In concentrated ammonia :			
Parabrombenzoic sulphinide	1.1	1.4	1.3
Potassium bromcyanbenzenesulphonate	3.6	3.4	3.3
2. In dilute ammonia (1 part conc. ammonia to 3 parts water) :			
Parabrombenzoic sulphinide	0.7	0.6	0.6
Potassium bromcyanbenzenesulphonate	3.4	3.8	3.5
3. In very dilute ammonia (1 part conc. ammonia to 20 parts water) :			
Parabrombenzoic sulphinide	0.28	0.26	0.31
Potassium bromcyanbenzenesulphonate	4.38	4.27	4.26

From the above table it will be seen that the more concentrated the ammonia the greater is the yield of the sulphinide.

The reaction by which the unsymmetrical chloride is converted into the ammonium salt of bromcyanbenzenesulphonic acid is expressed by the following equation :



[1] See page 504.

Whether another part of the unsymmetrical chloride is converted by the ammonia directly into the brombenzoic sulphinide, or is first changed into the symmetrical chloride, and then into the sulphinide, is not known.

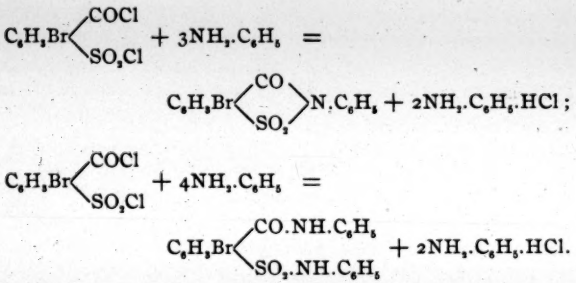
Aniline on the Symmetrical Chloride.—An emulsion of aniline and water was made by mixing 30 grams of aniline with 200 cc. of water in a large flask. To this mixture 25 grams of symmetrical chloride were slowly added. The chloride united at once with the aniline, forming a thick, yellowish, gummy substance, which, after being repeatedly shaken during twenty-four hours, had the appearance of a dark-brown powder. This was filtered off, washed first with cold, dilute hydrochloric acid, and then with water, and crystallized from alcohol. The product was placed on a perforated plate connected with a suction-pump, and slowly washed with a dilute solution of caustic soda until a portion of the filtrate collected in a test-tube no longer gave a precipitate when acidified with hydrochloric acid. The portion undissolved by the caustic soda was recrystallized from alcohol, from which it was obtained in long, slender needles, melting at 184° to 185°.

In accordance with the results obtained from a study of the chlorides of orthosulphobenzoic acid, this product must be regarded as the anil of parabromorthosulphobenzoic acid.

The filtrate containing the portion dissolved by the caustic soda, when acidified with hydrochloric acid, gave a white precipitate. This was collected and dissolved in boiling alcohol, from which it crystallized in short, silky needles. After being recrystallized several times, it showed a constant melting-point of 236° to 239°. This must be regarded as the symmetrical anilide of parabromorthosulphobenzoic acid.

The filtrate from the crude product obtained by the action of aniline on the symmetrical chloride was evaporated to a small volume, but yielded nothing but a small quantity of aniline hydrochloride.

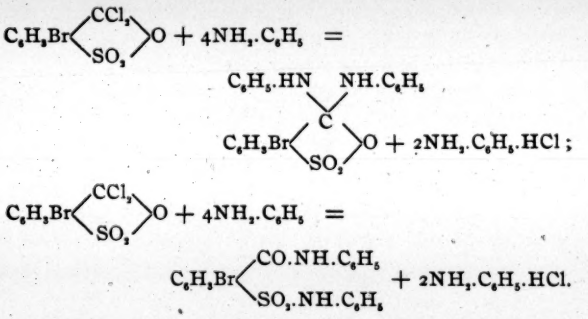
The anil and the anilide are formed in about equal proportions :



Aniline on the Unsymmetrical Chloride.—An emulsion of aniline in water was made as in the preceding experiment. Thirty grams of aniline were mixed with 200 cc. of water in a large glask. To this mixture 25 grams of the unsymmetrical chloride were slowly added. In this case also, the chloride united at once with the aniline, but the reaction was a much cleaner one than in the case of the symmetrical chloride. In the course of a few hours, after repeated shaking, the flask was found to contain a white, homogeneous powder. This was collected and boiled with alcohol. About half of the product finally went into solution. From the alcoholic solution a quantity of fine, silky needles was obtained, which, when recrystallized several times, melted at 236° to 239°. This is identical with the symmetrical anilide obtained from the symmetrical chloride as described above. The first alcoholic solution and the first lot of crystals were examined carefully for the anil, but no trace of it was found.

The product undissolved by the alcohol was dissolved by a dilute solution of caustic soda, from which it was immediately precipitated by the addition of hydrochloric acid. It was again treated with hot alcohol to remove any trace of the symmetrical anilide that might be present, again dissolved by the caustic soda, and again precipitated. This operation was repeated until a pure, perfectly white, amorphous substance was obtained which did not fuse at 300°, though it showed some indications of decomposing slightly below that tempera-

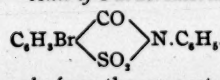
ture. This must be regarded as the unsymmetrical anilide. The anilides are formed in about equal proportions:



Here, also, it is not known whether a part of the unsymmetrical chloride is converted directly into the symmetrical anilide, or passes first, under the influence of the aniline, into the symmetrical chloride, and is then converted into the symmetrical anilide.

The above experiments were repeated several times, under the same conditions, and always with the same results. It will thus be seen that when aniline acts upon the chlorides in the cold, the symmetrical anilide and the anil are formed from the symmetrical chloride, while the symmetrical and unsymmetrical anilides are formed from the unsymmetrical chloride; in other words, the anil is obtained only from the symmetrical chloride, the unsymmetrical anilide only from the unsymmetrical chloride, while the symmetrical anilide is obtained from both. This was to be expected from the action of ammonia on the chlorides.

Anil of Parabromorthosulphobenzoic Acid,



—As has been said, the anil is obtained only from the symmetrical chloride. It is only slightly soluble in cold but easily soluble in hot alcohol, and readily soluble in benzene, chloroform, acetone, and glacial acetic acid.

From its alcoholic solution it crystallizes at first in long, slender needles, sometimes 45 mm. in length, but when these are recrystallized several times they assume the form of long, narrow, very thin plates. The anil melts at 184°.5.

0.2475 gram substance gave 0.1759 gram $BaSO_4$.

0.2451 gram substance gave 0.1696 gram $BaSO_4$.

0.2141 gram substance gave 0.00893 gram N.

0.2675 gram substance gave 0.01104 gram N.

0.1843 gram substance gave 0.3122 gram CO_2 and 0.0400 gram H_2O.

0.2141 gram substance gave 0.3601 gram CO_2 and 0.0514 gram H_2O.

	Calculated for $C_6H_3Br\langle^{CO}_{SO_2}\rangle N.C_6H_5$.	Found. I.	Found. II.
C	46.15	46.20	45.87
H	2.36	2.41	2.66
S	9.46	9.50	9.39
N	4.14	4.17	4.12

Symmetrical Anilide of Parabromorthosulphobenzoic Acid, $C_6H_3Br\langle^{CO.NH.C_6H_5}_{SO_2.NH.C_6H_5}$.—This substance is obtained both from the symmetrical and the unsymmetrical chloride. It is not soluble to any extent even in boiling alcohol, but is readily soluble in chloroform, acetone, benzene, and glacial acetic acid. It crystallizes in fine, silky needles. If the anilide in crystalline form is finely powdered and treated with a dilute solution of caustic soda, it goes into solution very slowly, nor will it be completely dissolved, however long it stands in contact with the alkali. The solution of the caustic soda, with whatever amount of the anilide it has dissolved, must be removed and a fresh portion of the alkali added, and this operation repeated a number of times, before the anilide is completely dissolved. Hydrochloric acid precipitates the anilide in amorphous form from its solution in caustic soda. The amorphous anilide is readily dissolved by the caustic soda. The symmetrical anilide melts at 236° to 239°, but if heated

rapidly to 238°, and if the source of heat is then removed, it will melt at 238° to 239°.

0.2357 gram substance gave 0.1343 gram $BaSO_4$.

0.1915 gram substance gave 0.1090 gram $BaSO_4$.

0.2949 gram substance gave 0.01922 gram N.

0.3176 gram substance gave 0.0207 gram N.

0.1919 gram substance gave 0.3699 gram CO_2 and 0.0631 gram H_2O.

0.2208 gram substance gave 0.4244 gram CO_2 and 0.0729 gram H_2O.

	Calculated for $C_6H_3Ba\langle^{CO.NH.C_6H_5}_{SO_3.NH.C_6H_5}$	Found. I.	II.
C	52.90	52.52	52.42
H	3.50	3.65	3.67
S	7.42	7.78	7.79
N	6.49	6.50	6.52

Unsymmetrical Anilide of Parabromorthosulphobenzoic Acid, $C_6H_5.HN \quad NH.C_6H_5$ $C_6H_3Br\langle^{C}_{SO_2}\rangle O$.—The unsymmetrical anilide is obtained only from the unsymmetrical chloride. It differs markedly from the symmetrical aniline in its behavior towards solvents. It is readily dissolved by a dilute solution of caustic soda, but is only slightly soluble in those other solvents in which the symmetrical anilide is easily dissolved. When it is boiled with absolute alcohol or with glacial acetic acid, it is dissolved to a slight extent, and if the solution is allowed to stand for several days the unsymmetrical anilide crystallizes out in fine, very short needles, which, like the amorphous form, do not fuse at 300°. Unlike the crystalline form of the symmetrical anilide, the crystals of the unsymmetrical anilide are dissolved at once upon the addition of dilute caustic soda.

0.1958 gram substance gave 0.1112 gram $BaSO_4$.

0.3118 gram substance gave 0.01675 gram N.

0.2085 gram substance gave 0.4040 gram CO_2 and 0.0690 gram H_2O.

	Calculated for $C_6H_3(SO_2)(C)(NH.C_6H_5)(N.C_6H_5)Br$	Found.
C	52.90	52.84
H	3.50	3.73
S	7.42	7.79
N	6.49	6.55

Action of Dehydrating Agents on the Symmetrical Anilide.

a. Phosphorus Pentoxide.—A mixture of the anilide and phosphorus pentoxide in the proportion of about 2 parts of the one to 5 parts of the other, was placed in a large test-tube closed with a cork stopper carrying a Bunsen valve, and heated to 180° for two hours. The anilide was partially transformed into a yellowish-brown substance, which dissolved readily in hot alcohol or glacial acetic acid. From these solvents it crystallized in dark-brown needles, melting at 200°.

In accordance with the work of Remsen and Hunter[1] on the anilides of orthosulphobenzoic acid, this must be regarded as the dianil of parabromorthosulphobenzoic acid formed from the anilide by elimination of the constituents of 1 molecule of water:

$$C_6H_3Br\begin{cases}CO.NH.C_6H_5\\SO_2.NH.C_6H_5\end{cases} = C_6H_3Br\begin{cases}C(=N.C_6H_5)\\SO_2\end{cases}N.C_6H_5 + H_2O.$$

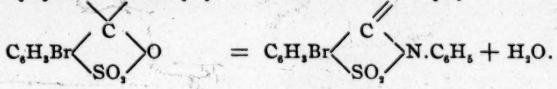
b. Phosphorus Oxychloride.—The symmetrical anilide was placed in a tubulated retort connected with a return condenser, and about ten times its weight of phosphorus oxychloride added. Sufficient heat was applied to bring the phosphorus oxychloride to gentle boiling. As soon as the liquid began to boil, a yellowish color made its appearance, and at the end of an hour all the anilide had reacted with the dehydrating agent, giving rise to a clear, dark-brown solution. The excess of phosphorus oxychloride was distilled off under diminished pressure, when a yellowish mass remained in the retort. This was washed with water, dried, and crystallized several

[1] This JOURNAL, 18, 809.

times from glacial acetic acid, when it was finally obtained in the form of small, bright-yellow plates, melting at 199° to 200°. This is the dianil, identical with the product obtained by the action of phosphorus pentoxide on the symmetrical anilide.

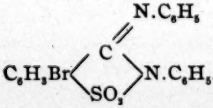
Action of Dehydrating Agents on the Unsymmetrical Anilide.

a. Phosphorus Pentoxide.—A mixture of equal parts of the unsymmetrical anilide and phosphorus pentoxide was heated to 180° in a closed test-tube for five hours. The same change was observed and the same product formed as in the case of the symmetrical anilide, but longer heating was required than was necessary with the latter.



b. Phosphorus Oxychloride.—The unsymmetrical anilide was boiled with phosphorus oxychloride in a tubulated retort connected with a return condenser. At the end of an hour, the anilide had completely dissolved, giving rise to a dark-brown solution. The excess of phosphorus oxychloride was distilled off under diminished pressure and the yellow residue crystallized from glacial acetic acid. Small, yellow crystals were obtained identical with the product from the reaction of phosphorus oxychloride on the symmetrical chloride.

Dianil of Parabromorthosulphobenzoic Acid,



.—As has just been stated, this substance can be prepared from both the symmetrical and the unsymmetrical anilide by the action of phosphorus pentoxide or of phosphorus oxychloride. It is obtained the more easily by the latter method. It must be regarded as formed by the abstraction of the constituents of 1 molecule of water from each molecule of the anilide. It is a beautiful, yellow compound, crystallizing from glacial acetic acid in small plates melting at

119° to 200°. It is readily soluble in alcohol, benzene, and chloroform. If a solution of the dianil in glacial acetic acid or in alcoholic potash is boiled for some time, it takes up one molecule of water and passes into the unsymmetrical anilide.

0.3836 gram substance gave 0.2169 gram $BaSO_4$.

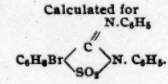
0.3195 gram substance gave 0.1831 gram $BaSO_4$.

0.2693 gram substance gave 0.0184 gram N.

0.2643 gram substance gave 0.01786 gram N.

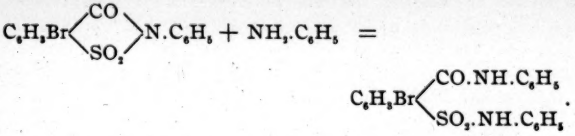
0.2141 gram substance gave 0.4324 gram CO_2 and 0.0646 gram H_2O.

0.2149 gram substance gave 0.4337 gram CO_2 and 0.0651 gram H_2O.

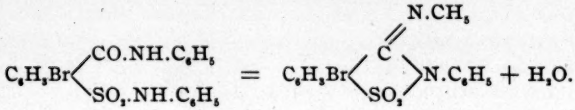
	Calculated for 	Found.	
		I.	II.
C	55.20	55.08	55.04
H	3.14	3.35	3.36
N	6.77	6.73	6.75
S	7.74	7.85	7.85

Transformation of the Anil into the Symmetrical Anilide.—Two grams of the anil were placed in a tubulated retort connected with a return condenser, and about ten times its weight of aniline added. Sufficient heat was applied to bring the aniline to gentle boiling. In an hour and a half the anil was completely dissolved, the solution being much darker than the original aniline. The solution was cooled and diluted with twenty times its volume of water, and the excess of aniline neutralized with hydrochloric acid. Upon the addition of the acid, a dark-brown product was precipitated. This was collected on a filter connected with a suction-pump, washed well with cold water, and then with a dilute solution of caustic soda as long as it continued to be dissolved by the alkali. In time it was almost completely dissolved, only a dark-brown, almost black, residue, being left on the filter. The alkaline filtrate was acidified with hydrochloric acid, and the white precipitate formed dissolved in hot alcohol. The product crystallized from the alcoholic solution in short, silky needles

melting at 235° to 239°. This proved it to be the symmetrical anilide:

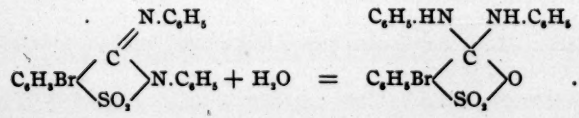


Transformation of the Symmetrical Anilide into the Dianil.—As has been described above, this transformation can easily be effected by heating the anilide with phosphorus pentoxide, or by boiling it with phosphorus oxychloride:

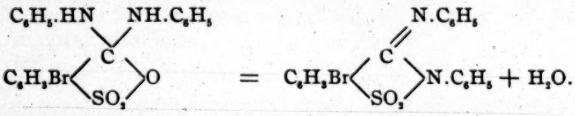


Transformation of the Dianil into the Unsymmetrical Anilide.—This can be accomplished by boiling a solution of the dianil in glacial acetic acid or in alcoholic potash. Into a 300 cc. round flask there were introduced 100 grams of alcohol, 2 grams of caustic potash, and 2 grams of the dianil. The flask was connected with a return condenser and the solution boiled for two hours. Most of the alcohol was then distilled off and the remaining solution diluted with water. The solution was acidified with hydrochloric acid. The precipitate, which was immediately formed, proved to be the unsymmetrical anilide.

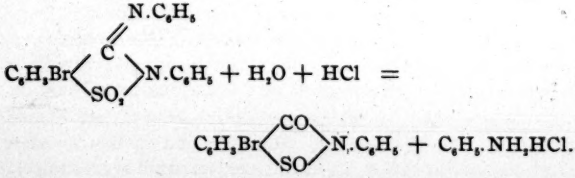
A small quantity of the dianil was dissolved in hot glacial acetic acid and the solution boiled for half an hour. After the solution had cooled, the unsymmetrical anilide crystallized out in very short needles along with some of the unchanged dianil:



Transformation of the Unsymmetrical Anilide into the Dianil.—As has already been described, this transformation is easily effected by heating the unsymmetrical anilide with phosphorus pentoxide or by boiling it with phosphorus oxychloride:

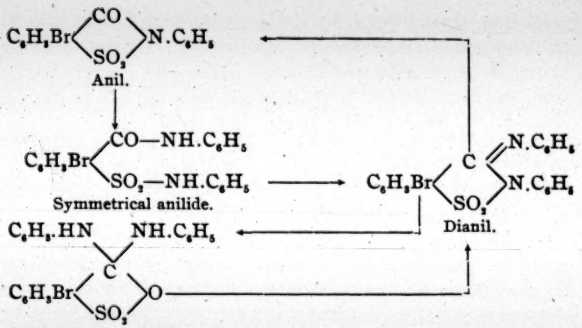


Transformation of the Dianil into the Anil.—Two grams of finely powdered dianil were placed in a tubulated retort connected with a return condenser, and about 100 grams of concentrated hydrochloric acid added. The acid was then boiled. As soon as the boiling began, the yellow color of the dianil began to grow fainter, and in an hour and a half it had completely disappeared. The undissolved contents of the retort were transferred to a beaker, diluted with water, filtered, and washed free from hydrochloric acid. The product was dissolved in alcohol, from which it crystallized in needles melting at 184° to 185°. This proved to be the anil of parabromorthosulphobenzoic acid:



It will be readily seen that the above transformations are identical with those described by Remsen and Hunter[1] in the case of the corresponding compounds from orthosulphobenzoic acid. They may be graphically represented by the following diagram:

[1] *Loc. cit.*



The above transformations suggested the possibility of passing directly from one chloride to the other. Since in the preparation of the unsymmetrical chloride none of the symmetrical compound is every found, it seemed possible that this chloride might be transformed into the other by heating with phosphorus oxychloride.

Five grams of the symmetrical chloride were heated with several times its weight of phosphorus oxychloride in a sealed tube at 130° for five hours. The phosphorus oxychloride was then distilled off under diminished pressure and the residue crystallized from ligroin. The crystals melted at the same temperature as before heating, showing that no change had taken place.

Portions of each chloride were next heated in sealed tubes in a sulphuric acid-bath at 106° for three days. As long as the temperature remained above 100°, both chlorides remained in the liquid state. At the end of three days the tubes were opened. In each there was noticed the odor of hydrochloric acid. Upon the walls of each tube was found a small quantity of a sublimate which had collectly mostly in the form of fine needles. That from the symmetrical compound melted at 99°, the melting-point of the symmetrical chloride, that from the unsymmetrical compound, melted at 89°, the melting-point of the unsymmetrical chloride. The products in the tubes

were then crystallized from ligroin, and one was found to be the unchanged symmetrical chloride, and the other the unchanged unsymmetrical chloride.

Summary.

By the experiments recorded above, the following facts are established:

1. With the higher melting chloride, ammonia gives only one product, parabrombenzoic sulphinide.

2. With the lower melting chloride, ammonia gives two products, parabrombenzoic sulphinide and ammonium parabromorthocyanbenzenesulphonate, the proportion of the former decreasing with the dilution of the ammonia, being 26 per cent with concentrated ammonia, 15 per cent with dilute ammonia (1 to 3), and 6 per cent with very dilute ammonia (1 to 20).

3. Aniline in the cold gives with the higher melting chloride two products, the anil and the fusible anilide.

4. Aniline in the cold gives with the lower melting chloride two products, the fusible and infusible anilides.

5. Dehydrating agents convert the anilides into a dianil, and only one dianil is known.

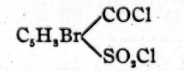
6. Passage can readily be effected from the anil on the one side to the infusible aniline on the other by passing through the fusible anilide and the dianil. On the other hand, the infusible anilide can readily be converted into the anil through the dianil.

7. The higher melting chloride is unchanged when heated in a sealed tube with phosphorus oxychloride at 130°, and neither chloride is appreciably decomposed when kept in the liquid state in a sealed tube for several days.

These results are in accordance with those published by Professor Remsen and some of his students in this JOURNAL upon the chlorides of orthosulphobenzoic acid, to which references have already been made, and are not in accordance with the statements of List and Stein,[1] to which reference has also been made. It seems that these chlorides are isomeric and not tautomeric substances, that they are separate and distinct

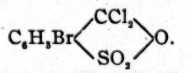
[1] *Loc. cit.*

from each other, and that each is as much entitled to its individual constitutional formula as any other stable chemical compound is. Evidence points to the symmetrical structure for the higher melting chloride, and to the unsymmetrical structure for the lower melting chloride. These compounds should, therefore, be represented thus :



Symmetrical chloride.

and

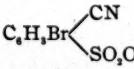


Unsymmetrical chloride.

PART II.

The remainder of this article will be devoted to a description of the properties and some of the derivatives of three acids obtained either directly or indirectly from the chlorides. Of these acids, parabromorthocyanbenzenesulphonic acid and parabromorthocarbaminesulphonic acid come from the unsymmetrical chloride, and parabromorthosulphaminebenzoic acid comes from the symmetrical chloride. The results of a further study of parabrombenzoic sulphinide will also be included here.

Parabromorthocyanbenzenesulphonic Acid,



.—As has been said, when the unsymmetrical chloride is dissolved in ammonia, the main product of the reaction is the ammonium salt of parabromorthocyanbenzenesulphonic acid. This can readily be converted into the barium salt, from which the free acid can be obtained by precipitating the barium. It can also be prepared by boiling with water parabromorthocyansulphone chloride, which is one of the products of the action of phosphorus pentachloride upon parabrombenzoic sulphinide. The acid is very soluble in water. When an aqueous solution of the acid is boiled for five hours with dilute hydrochloric acid it remains unchanged; when, however, its alkali salts are boiled for five hours with dilute sodium hydroxide or potassium hydroxide they are converted into the sodium or the potassium salt of parabromor-

thocarbaminesulphonic acid, and, if the boiling is continued ten hours longer, they are partially converted into the corresponding salts of parabromorthosulphobenzoic acid. The changes are represented as follows:

1. $C_6H_3Br\begin{cases}CN\\SO_2OK\end{cases} + H_2O + C_6H_3Br\begin{cases}CONH_2\\SO_2OK\end{cases}$;

2. $C_6H_3Br\begin{cases}CONH_2\\SO_2OK\end{cases} + H_2O + KOH = C_6H_3Br\begin{cases}COOK\\SO_2OK\end{cases} + NH_3 + H_2O.$

The other salts of the acid are easily prepared by starting with the ammonium salt.

Ammonium Parabromorthocyanbenzenesulphonate, $C_6H_3Br\begin{cases}CN\\SO_2ONH_4\end{cases}$.—This salt was obtained by dissolving the unsymmetrical chloride in ammonia. It is very soluble in water, much less soluble in alcohol. From its aqueous solution it crystallizes in small, lustrous plates, which have an extremely bitter taste.

0.3630 gram substance gave 0.2183 gram NH_3.

0.3081 gram substance gave 0.1847 gram NH_3.

	Calculated for $C_6H_3Br\begin{cases}CN\\SO_2ONH_4\end{cases}$.	Found. I.	Found. II.
NH_3	6.09	6.01	6.00

Potassium Parabromorthocyanbenzenesulphonate, $C_6H_3Br\begin{cases}CN\\SO_2OK\end{cases} + 1\frac{1}{2}H_2O$.—The potassium salt was made by adding a solution of potassium carbonate or potassium hydroxide to a solution of the ammonium salt. The potassium salt, being much less soluble than the ammonium salt, is precipitated. It is readily soluble in hot water, but much less soluble in cold. From its aqueous solution it crystallizes in fine, silky needles having a bitter taste.

0.1947 gram substance lost 0.0160 gram H_2O.
0.1909 gram substance lost 0.0158 gram H_2O.
0.1947 gram substance gave 0.0513 gram K_2SO_4.
0.1909 gram substance gave 0.0504 gram K_2SO_4.

	Calculated for $C_6H_3Br\langle^{CN}_{SO_3OK} + 1\frac{1}{2}H_2O$.	Found. I.	II.
H_2O	8.25	8.22	8.27
K	11.92	11.80	11.83

Sodium Parabromorthocyanbenzenesulphonate, $C_6H_3Br\langle^{CN}_{SO_3ONa} + 1\frac{1}{2}H_2O$.—The sodium salt was made by adding a solution of sodium carbonate or sodium hydroxide to a fairly concentrated solution of the ammonium salt. It is much more soluble in hot than in cold water, and crystallizes in long, silky needles, resembling the potassium salt.

0.2379 gram substance lost 0.0209 gram H_2O.
0.2178 gram substance lost 0.0189 gram H_2O.
0.2379 gram substance gave 0.0530 gram Na_2SO_4.
0.2178 gram substance gave 0.0492 gram Na_2SO_4.

	Calculated for $C_6H_3Br\langle^{CN}_{SO_3ONa} + 1\frac{1}{2}H_2O$.	Found. I-	II.
H_2O	8.68	8.76	8.72
Na	7.39	7.21	7.31

Barium Parabromorthocyanbenzenesulphonate, $\left(C_6H_3Br\langle^{CN}_{SO_3O}\right)_2Ba + 6H_2O$.—The barium salt was prepared by adding a warm, saturated solution of barium hydroxide to a hot, concentrated solution of the ammonium salt. When the mixture cooled, the barium salt, mixed with some of the ammonium salt, crystallized out of the solution in long needles. After several crystallizations it was obtained quite pure in long, lustrous, rectangular plates.

It can also be prepared by neutralizing the free acid with barium carbonate. In this way it was once obtained crystal-

lizing in prisms with 3 molecules of water, as will be described later.

If a solution of barium hydroxide is added to a dilute solution of the ammonium salt, and an attempt is made to obtain the barium salt by evaporating the solution, a basic salt will be precipitated. This is very difficultly soluble in cold or hot water, and contains between 36 and 37 per cent of barium.

0.3166 gram substance gave 0.1947 gram $BaSO_4$.

An analysis of the pure barium salt gave the following results:

0.2803 gram substance lost 0.0396 gram H_2O.
0.2554 gram substance lost 0.0359 gram H_2O.
0.2803 gram substance gave 0.0855 gram $BaSO_4$.
0.2554 gram substance gave 0.0779 gram $BaSO_4$.

	Calculated for $\left(C_6H_3Br\langle^{CN}_{SO_3O}\right)_2Ba + 6H_2O$.	Found. I.	II.
H_2O	14.08	14.13	14.05
Ba	17.86	17.94	17.90

Magnesium Parabromorthocyanbenzenesulphonate, $\left(C_6H_3Br\langle^{CN}_{SO_3O}\right)_2Mg + 8\frac{1}{2}H_2O$.—The magnesium salt was made by adding to a solution of the barium salt just enough magnesium sulphate to precipitate all the barium. It is readily soluble in hot water, much less soluble in cold, and from its aqueous solution crystallizes in diamond-shaped tables, the crystals often having a hopper appearance.

0.2258 gram substance lost 0.0493 gram H_2O.
0.2267 gram substance lost 0.0492 gram H_2O.
0.2073 gram substance lost 0.0448 gram H_2O.
0.2258 gram substance gave 0.0374 gram $MgSO_4$.
0.2267 gram subsrance gave 0.0382 gram $MgSO_4$.
0.2073 gram substance gave 0.0349 gram $MgSO_4$.

	Calculated for $\left(C_6H_3Br\langle^{CN}_{SO_3O}\right)_2Mg + 8\frac{1}{2}H_2O$.	Found. I.	II.	III.
H_2O	21.88	21.88	21.71	21.61
Mg	3.43	3.31	3.37	3.36

The zinc salt was also prepared. It crystallizes in small plates, and, like the magnesium salt, contains 8.5 molecules of water of crystallization.

Copper Parabromorthocyanbenzenesulphonate, $\left(C_6H_3Br\begin{smallmatrix}CN\\SO_3O\end{smallmatrix}\right)_2Cu + 4H_2O$.—The copper salt was made from the barium salt by precipitating the barium with pure copper sulphate. It crystallizes in fine needles or long, thin plates of a delicate blue color. It is very soluble in water.

0.2230 gram substance lost 0.0242 gram H_2O.
0.2046 gram substance lost 0.0221 gram H_2O.
0.2046 gram substance gave 0.0233 gram CuO.

	Calculated for $\left(C_6H_3Br\begin{smallmatrix}CN\\SO_3O\end{smallmatrix}\right)_2Cu + 4H_2O$.	Found. I.	II.
H_2O	10.90	10.85	10.81
Cu	9.58	....	9.22

Parabromorthocarbaminebenzenesulphonic Acid, $C_6H_3Br\begin{smallmatrix}CONH_2\\SO_3OH\end{smallmatrix}$.—The free acid was not obtained and only the sodium and potassium salts were prepared. When these are boiled for ten hours with dilute sodium hydroxide or potassium hydroxide they are partly converted into the corresponding salts of parabromorthosulphobenzoic acid:

$$C_6H_3Br\begin{smallmatrix}CONH_2\\SO_3OK\end{smallmatrix} + H_2O + KOH = C_6H_3Br\begin{smallmatrix}COOK\\SO_3OK\end{smallmatrix} + H_2O + NH_3.$$

Sodium Parabromorthocarbaminebenzenesulphonate, $C_6H_3Br\begin{smallmatrix}CONH_2\\SO_3ONa\end{smallmatrix} + \frac{1}{2}H_2O$.—This salt was prepared by boiling for five hours a solution of ammonium or sodium parabromorthocyanbenzenesulphonate with dilute sodium hy-

droxide. The solution was filtered, evaporated to a small volume, and allowed to stand for several days over sulphuric acid, when the sodium parabromorthocarbaminesulphonate crystallized out in short needles in wart-like clusters. The salt is very soluble in water.

0.2041 gram substance lost 0.0066 gram H_2O.
0.1919 gram substance lost 0.0055 gram H_2O.
0.2041 gram substance gave 0.0462 gram Na_2SO_4.
0.1919 gram substance gave 0.0439 gram Na_2SO_4.

	Calculated for $C_6H_3Br\begin{cases}CONH_2\\SO_2ONa\end{cases} + \frac{1}{2}H_2O$.	Found. I.	Found. II.
H_2O	3.07	2.93	2.86
Na	7.40	7.33	7.41

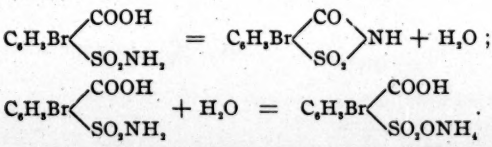
Potassium Parabromorthocarbaminebenzenesulphonate, $C_6H_3Br\begin{cases}CONH_2\\SO_2OK\end{cases}$.—The potassium salt was made by boiling for five hours a solution of ammonium or potassium parabromorthocyanbenzenesulphonate with dilute potassium hydroxide. The solution was filtered, evaporated to a small volume, and allowed to stand for several days, when the potassium parabromorthocarbaminesulphonate crystallized out in short needles, radiating from a common center.

0.1746 gram substance gave 0.0479 gram K_2SO_4.
0.2011 gram substance gave 0.0552 gram K_2SO_4.
0.1729 gram substance gave 0.0471 gram K_2SO_4.

	Calculated for $C_6H_3Br\begin{cases}CONH_2\\SO_2OK\end{cases}$	Found. I.	Found. II.	Found. III.
K	12.26	12.36	12.33	12.24

Parabromorthosulphaminebenzoic Acid, $C_6H_3Br\begin{cases}COOH\\SO_2NH_2\end{cases}$.—This acid is easily prepared by hydrolyzing parabrombenzoic sulphinide. Fifteen grams of the sulphinide were placed in a liter balloon flask containing 0.5 liter of water and attached to a return condenser. A little more potassium hydroxide was added than was necessary to neutralize the sulphinide.

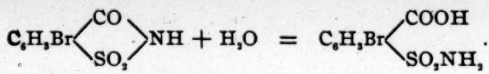
Heat was applied and the solution kept gently boiling for five hours. It was then filtered off, and after it had cooled enough hydrochloric acid was added to precipitate all the sulphamine acid. The acid crystallizes in long, very thin, lustrous plates. It is readily soluble in hot water, but only slightly soluble in cold. It has no sharp melting-point, but after being recrystallized several times it melts constantly at 192° to 197°. When heated to 127° in a covered crucible, it begins to lose water of constitution and pass over partly into parabrombenzoic sulphinide, which collects in the top of the crucible; but this water unites with another portion of the sulphamine acid, converting it into the acid ammonium salt of parabromorthosulphobenzoic acid, which does not sublime, but remains in the base of the crucible. A portion of the sulphamine acid was heated for thirty hours at 160°. It was weighed from time to time and found to be diminishing in weight at the rate of about a milligram every three hours. At the end of the thirty hours only a small quantity of the sulphinide had collected in the top of the crucible. The product in the base of the crucible was comparatively pure acid ammonium parabromorthosulphobenzoate. Hence the loss in weight was due largely to the subliming of the sulphinide out of the crucible. The changes here described are represented as follows:



When the free sulphamine acid is boiled with dilute hydrochloric acid, it passes rapidly over into the acid ammonium salt of parabromorthosulphobenzoic acid, but if the alkali salts of the acid are boiled with dilute alkalies this hydrolysis does not take place even when the heating is continued for ten hours.

Parabromorthosulphaminebenzoic acid can be prepared also by boiling parabrombenzoic sulphinide with dilute hydro-

chloric acid, provided the heating is not continued longer than forty-five minutes :



If the boiling is carried on for a longer time, the product is the acid ammonium salt of parabromorthosulphobenzoic acid.

The salts of the sulphamine acid are more soluble in water than the free acid. They are prepared in the usual way. When heated above 150°, they pass over into the corresponding salts of parabrombenzoic sulphinide.

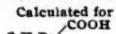
The alkali salts are very soluble. The strontium, barium, magnesium, and calcium salts, in their solubility, follow each other in the order named, the calcium salt being but slightly soluble in water.

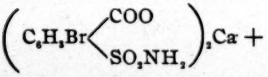
An analysis of the free acid gave the following results :

0.2439 gram substance gave 0.2026 gram $BaSO_4$.

0.2195 gram substance gave 0.01103 gram N.

0.2427 gram substance gave 0.01129 gram N.

	Calculated for 	Found. I.	II.	III.
S	11.42	11.38	....	....
N	5.00	....	5.02	5.06

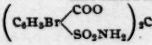
Calcium Parabromorthosulphaminebenzoate,  —The calcium salt crystallizes slowly from its aqueous solution in large prisms having hemihedral faces.

0.2381 gram substance lost 0.0135 gram H_2O.

0.2737 gram substance lost 0.0127 gram H_2O.

0.2381 gram substance gave 0.0513 gram $CaSO_4$.

0.2237 gram substance gave 0.0482 gram $CaSO_4$.

	Calculated for 	Found. I.	II.
H_2O	5.67	5.67	5.67
Ca	6.41	6.33	6.33

Strontium Parabromorthosulphaminebenzoate,

$\left(C_6H_3Br\begin{matrix}COO\\SO_2NH_2\end{matrix}\right)_2Sr + 4H_2O$. — The strontium salt is much more soluble than the calcium salt. From its aqueous solution it crystallizes in long, slender needles.

0.2048 gram substance lost 0.0210 gram H_2O.
0.2237 gram substance lost 0.0230 gram H_2O.
0.2048 gram substance gave 0.0529 gram $SrSO_4$.
0.2237 gram substance gave 0.0570 gram $SrSO_4$.

	Calculated for $\left(C_6H_3Br\begin{matrix}COO\\SO_2NH_2\end{matrix}\right)_2Sr + 4H_2O$.	Found. I.	II.
H_2O	10.04	10.25	10.28
Sr	12.17	12.30	12.13

Barium Parabromorthosulphaminebenzoate,

$\left(C_6H_3Br\begin{matrix}COO\\SO_2NH_2\end{matrix}\right)_2Ba + 2H_2O$.—The barium salt is readily soluble in hot water, much less soluble in cold. From its aqueous solution it crystallizes in short needles.

0.2583 gram substance lost 0.0124 gram H_2O.
0.2157 gram substance lost 0.0104 gram H_2O.
0.2234 gram substance gave 0.0716 gram $BaSO_4$.
0.2157 gram substance gave 0.0685 gram $BaSO_4$.

	Calculated for $\left(C_6H_3Br\begin{matrix}COO\\SO_2NH_2\end{matrix}\right)_2Ba + 2H_2O$.	Found. I.	II.
H_2O	4.92	4.80	4.82
Ba	18.73	18.85	18.67

Sodium Parabromorthosulphaminebenzoate,

$C_6H_3Br\begin{matrix}COONa\\SO_2NH_2\end{matrix}$.—The sodium salt is very soluble in water. After standing over sulphuric acid it crystallizes in short needles from the concentrated solution.

0.2084 gram substance gave 0.0493 gram Na_2SO_4.
0.2582 gram substance gave 0.0612 gram Na_2SO_4.

	Calculated for $C_6H_3Br\langle^{COONa}_{SO_2NH_2}$.	Found. I.	II.
Na	7.61	7.66	7.67

Potassium Parabromorthosulphaminebenzoate, $C_6H_3Br\langle^{COOK}_{SO_2NH_2}$.—The potassium salt is very soluble even in cold water, but not so soluble as the sodium salt. On standing over sulphuric acid, it crystallizes from a concentrated solution in large, rectangular plates, often arranged in clusters.

0.2015 gram substance gave 0.0553 gram K_2SO_4.
0.2365 gram substance gave 0.0650 gram K_2SO_4.

	Calculated for $C_6H_3Br\langle^{COOK}_{SO_2NH_2}$.	Found. I.	II.
K	12.26	12.29	12.31

Magnesium Parabromorthosuphaminebenzoate, $\left(C_6H_3Br\langle^{COO}_{SO_2NH_2}\right)_2Mg + 3H_2O$.—The magnesium salt was prepared from the barium salt by adding magnesium sulphate to precipitate all the barium. It crystallizes in short needles arranged in tufts.

0.2807 gram substance lost 0.0241 gram H_2O.
0.2099 gram substance lost 0.0180 gram H_2O.
0.2476 gram substance gave 0.0454 gram $MgSO_4$.
0.2807 gram substance gave 0.0511 gram $MgSO_4$.
0.2099 gram substance gave 0.0390 gram $MgSO_4$.

	Calculated for $\left(C_6H_3Br\langle^{COO}_{SO_2NH_2}\right)_2Mg + 3H_2O$.	Found. I.	II.	III.
H_2O	8.49	8.58	8.57	....
Mg	3.77	3.66	3.64	3.71

The copper salt was also prepared. It is insoluble in water and is precipitated in the form of very fine needles when a solution of copper sulphate is added to a soluble salt of the

sulphamine acid. When dry, the salt is very light, has a delicate bluish color, and exhibits magnetic properties.

Action of Phosphorus Pentachloride on Parabrombenzoic Sulphinide.

Twenty grams of parabrombenzoic sulphinide were mixed with an equal quantity of phosphorus pentachloride and heated in sealed tubes for five hours at 180°. The product of the reaction was a clear, dark-brown, oily substance, which solidified soon after being poured into cold water. The solid product was filtered off, washed thoroughly, and dried. It had the characteristic odor of nitriles. Five grams of this product were placed in a small, round-bottomed flask containing 30 grams of concentrated sulphuric acid and 10 grams of water, the flask was connected with an upright condenser, and the mixture gently heated until a quantity of needle-like crystals had sublimed in the neck of the flask. The mixture was allowed to cool, when a substance crystallized out in the form of needles. These were collected on an asbestos filter and dissolved in hot water. When the solution cooled, only a small quantity of the product crystallized out. This appeared in the form of needles and proved to be parabromorthochlorbenzoic acid, first made by Willgerodt and Salzmann.[1] The filtrate from these crystals was evaporated to a small volume, and on cooling solidified almost entirely in the form of a crystalline mass. This was found to be parabromorthosulphobenzoic acid, as was proved by neutralizing a portion with potassium hydroxide and adding to the concentrated solution a small quantity of hydrochloric acid. The acid potassium salt was precipitated in small, lustrous plates. Upon analysis, 0.3027 gram salt gave 0.0828 gram K_2SO_4.

	Calculated for $C_6H_3Br\begin{cases}COOH\\SO_2OK\end{cases}$.	Found.
K	12.22	12.27

When the free acid is recrystallized several times it can be obtained in large, rectangular plates, melting at 117°.

[1] J. prakt. Chem. [2], **39**, 470 (1889).

Another portion of the product obtained from the action of phosphorus pentachloride on the brombenzoic sulphinide was subjected to distillation with steam. A product distilled over, having the odor of nitriles and collecting in fine needles. This was proved to be parabromorthochlorbenzoic nitrile by hydrolyzing it in sealed tubes with hydrochloric acid. It was converted into parabromorthochlorbenzoic acid.

When, in the distillation with steam, the nitrile ceased to come over, the solution in the flask was evaporated to a small volume. On cooling, this solidified into a slightly yellowish, amorphous substance. It was found to give an acid reaction. A portion of it was dissolved in water and neutralized with barium carbonate. The excess of barium carbonate was removed and the clear solution allowed to stand several days. During this time a salt crystallized out in the form of prisms, which, when recrystallized, came out in the same form, and upon analysis proved to be barium parabromorthocyanbenzenesulphonate with 3 molecules of water of crystallization.

0.2824 gram substance lost 0.0212 gram H_2O.
0.2640 gram substance lost 0.0197 gram H_2O.
0.2624 gram substance gave 0.0912 gram $BaSO_4$.
0.2640 gram substance gave 0.0854 gram $BaSO_4$.

	Calculated for $\left(C_6H_3Br\begin{smallmatrix}CN\\SO_2O\end{smallmatrix}\right)_2Ba + 3H_2O$.	Found. I.	Found. II.
H_2O	7.57	7.50	7.46
Ba	19.11	19.03	19.03

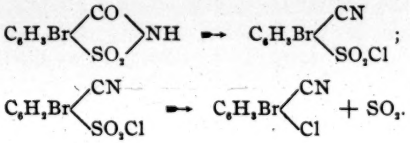
The potassium salt was also made. It was identical with the potassium parabromorthocyanbenzenesulphonate obtained from the corresponding ammonium salt, as has already been described.

0.1537 gram substance lost 0.0128 gram H_2O.
0.1537 gram substance gave 0.0410 gram K_2SO_4.

	Calculated for $C_6H_3Br\begin{smallmatrix}CN\\SO_2OK\end{smallmatrix} + 1\frac{1}{2}H_2O$.	Found.
H_2O	8.25	8.32
K	11.92	11.95

An attempt to obtain the barium salt in the above form from a second lot of the acid did not prove successful. The salt crystallized in needles, and was very soluble in water.

The results of the above experiment indicate quite clearly that when phosphorus pentachloride and parabrombenzoic sulphinide are heated in sealed tubes two products are formed, parabromorthocyanbenzenesulphone chloride and parabromorthochlorbenzoic nitrile. Further investigation proved this to be the case. It was found that when the temperature is not allowed to rise higher than 150°, the main product of the reaction is the bromcyansulphone chloride; when the temperature is raised to 200°, the larger part of the product is bromchlorbenzoic nitrile. The reaction probably takes place in two stages:



When the tubes that had been heated to 200° were opened there was always present a strong odor of sulphur dioxide.

Parabromorthocyanbenzenesulphone Chloride, $C_6H_3Br\begin{cases}CN\\SO_2Cl\end{cases}$.—This compound is easily prepared by heating parabrombenzoic sulphinide with an equal quantity of phosphorus pentachloride in sealed tubes at 150°. It can be separated from the nitrile accompanying it by crystallizing it several times from ligroin. It is readily soluble in hot ligroin, but only slightly soluble in cold. It is very soluble in benzene and glacial acetic acid. When crystallized several times from ligroin it can be obtained in perfectly white plates, having no odor and melting at 82°. When boiled with water it is readily converted into parabromorthocyanbenzenesulphonic acid, and when heated with slightly diluted sulphuric acid it is converted into parabromorthosulphobenzoic acid.

0.2470 gram substance gave 0.2755 gram CO_2 and 0.0296 gram H_2O.

0.1678 gram substance gave 0.1963 gram of a mixture of AgCl and AgBr.

0.1896 gram substance gave 0.2215 gram of a mixture of AgCl and AgBr.

0.2822 gram substance gave 0.01401 gram N.

0.3224 gram substance gave 0.1625 gram N.

0.1678 gram substance gave 0.1422 gram $BaSO_4$.

0.1896 gram substance gave 0.1593 gram $BaSO_4$.

	Calculated for $C_6H_3Br\begin{cases}CN\\SO_2Cl\end{cases}$.	Found. I.	Found. II.
C	29.94	30.41	....
H	1.06	1.33	....
S	11.41	11.63	11.53
N	4.99	4.97	5.04
Cl, Br	41.17	40.75	40.70

Parabromorthochlorbenzoic Nitrile, $C_6H_3Br\begin{cases}CN\\Cl\end{cases}$.—This compound is readily obtained by heating parabrombenzoic sulphinide with an equal weight of phosphorus pentachloride in sealed tubes at 200°, and distilling the product with steam. The nitrile is volatile with steam and collects in the receiver in the form of fine, white needles. It is very soluble in benzene, glacial acetic acid, and ligroin. The product distilled over with steam, melts at 51° to 61°, and the melting-point is not changed when it is redistilled. When the nitrile is heated either in sealed tubes with hydrochloric acid or in a flask with sulphuric acid containing a little water, it is converted into parabromorthochlorbenzoic acid.

0.2439 gram substance gave 0.3486 gram CO_2 and 0.0324 gram H_2O.

0.2252 gram substance gave 0.3195 gram CO_2 and 0.0278 gram H_2O.

0.2579 gram substance gave 0.0161 gram N.

0.3286 gram substance gave 0.02057 gram N.

0.1885 gram substance gave 0.2850 gram mixture AgCl and AgBr.

	Calculated for $C_6H_3Br\begin{cases}CN\\Cl\end{cases}$	Found. I.	II.
C	38.80	38.08	38.70
H	1.38	1.47	1.37
N	6.46	6.24	6.27
Cl } Br }	53.34	52.67	....

Summary.

The principal results recorded in the second part of this article may be summed up as follows:

1. When parabromorthocyanbenzenesulphonic acid is boiled with dilute hydrochloric acid, it is not changed. If, however, it is boiled with a slight excess of potassium hydroxide or sodium hydroxide, it is converted into the potassium or the sodium salt of parabromorthocarbaminesulphonic acid.

2. When parabrombenzoic sulphinide is boiled with dilute hydrochloric acid for forty-five minutes, it is converted into parabromorthosulphaminebenzoic acid. When it is boiled with a slight excess of potassium hydroxide for five hours, it is converted into the potassium salt of parabromorthosulphaminebenzoic acid.

3. When the alkali salts of parabromorthocarbaminesulphonic acid are boiled for ten hours with dilute alkalies they are partly converted into the corresponding salts of parabromorthosulphobenzoic acid.

4. When parabromorthosulphaminebenzoic acid is boiled with dilute hydrochloric acid, it is readily converted into the acid ammonium salt of parabromorthosulphobenzoic acid. When it is boiled with a slight excess of potassium hydroxide it is not changed.

5. When parabrombenzoic sulphinide is heated with phosphorus pentachloride in sealed tubes at 150°, the main portion of the product is parabromorthocyansulphone chloride. If the temperature is raised to 200°, the larger proportion of the product is parabromorthochlorbenzoic nitrile.

Contributions from the Chemical Laboratory of Harvard College.

ON THE ACTION OF ANILINE UPON TETRABROMORTHOBENZOQUINONE.[1]

By C. Loring Jackson and Horace C. Porter.

In continuing the work on orthoquinone, begun by Koch and one of us[2] a few years ago, we have studied the action of aniline on the tetrabromorthobenzoquinone, and have found that if the reaction is carried on in alcoholic solution the first product must be dianilinodibromorthoquinone. This substance, however, does not appear as one of the products of the reaction, because of its great tendency to form addition-compounds, so that the first product of the reaction is its compound with aniline,

$$C_6Br_2(C_6H_5NH)_2O_2C_6H_5NH_2,$$

pale-brown needles, melting with decomposition at 121° to 124°, while later there is obtained its compound with alcohol,

$$C_6Br_2(C_6H_5NH)_2O_2C_2H_5OH,$$

yellow plates melting with decomposition at 142°, or, if methyl alcohol is used as a diluent, the corresponding methyl compound, which melts at 144° to 145°. These addition-products are decidedly unstable, the aniline derivative being converted into the alcohol compound by standing for a few minutes with alcohol in the cold. They are also slowly decomposed at temperatures as low as 60°, and by digestion at about 50° with a mixture of benzol and ligroin. They can, on the other hand, be recrystallized from benzol without decomposition, and we ascribe this difference to the fact that the dianilinodibromorthoquinone is but slightly soluble in the mixture of benzol and ligroin, whereas it is freely soluble in benzol alone.[3]

The best method of obtaining the dianilinodibromorthobenzoquinone, $C_6Br_2(C_6H_5NH)_2O_2$, is by repeatedly digesting

[1] The work described in this paper formed part of a thesis presented to the Faculty of Arts and Sciences of Harvard University for the degree of Doctor of Philosophy, by Horace C. Porter.

[2] This Journal, 26, 10 (1901).

[3] Compare the similar phenomena observed by Niemeyer with nitroaniline and chlorquinones. Ann. Chem. (Liebig), 228, 324 (1885).

its aniline compound with a mixture of benzol and ligroin. It crystallizes in dark, reddish-purple needles and melts at 160°. It combines easily with aniline dissolved in benzol, or with ethyl alcohol to form the addition-compounds already described.

The very slight stability of these addition-compounds makes it probable that they are hemiacetals, or the corresponding compound formed by the addition of a molecule of aniline to one carbonyl group, and this view of their constitution is in harmony with the work of Zincke and Arnst,[1] Zincke and Neumann,[2] and Zincke and Schaum,[3] which has proved the existence of hemiacetals derived from other substituted orthoquinones, but, if they are hemiacetals, it is strange that the addition is confined to one of the carbonyl groups. We hope that in the coming year this hypothesis in regard to our substances may be tested experimentally in this laboratory.

If the dianilinodibromorthobenzoquinone or any of its addition-compounds is left standing with a mixture of aniline or an aniline salt and alcohol, or boiled for a few minutes with such a mixture, a new substance is formed crystallizing in very brilliant, jet-black plates and melting at 173°, which proved, on analysis, to be a dianilinobromquinoneanil. This is the substance obtained by Zincke[4] from the action of aniline on tetrabromorthobenzoquinone, but not analyzed by him. As the method of preparation shows, it is much more stable than the compounds previously mentioned in this paper, and is, in fact, the usual product of the reaction of aniline on tetrabromorthoquinone when no special precautions are taken to stop the action at the derivatives of dianilinodibromorthoquinone. The stability of this black compound suggests the idea that it may be a derivative of paraquinone, and this is essentially proved to be the case by the fact that an ethereal solution of sulphurous dioxide converts it in the cold into the known dianilinoparaquinoneanil melting at 202° to 203°. As it is hardly possible to suppose that the change from the ortho

[1] Ann. Chem. (Liebig), **267**, 319 (1892).
[2] *Ibid.*, **278**, 173 (1894).
[3] Ber. d. chem. Ges., **27**, 537 (1894).
[4] *Ibid.*, **20**, 1778 (1887).

to the para series would have taken place under such conditions, we are led to the conclusion that the black substance is already a para compound, and that the action of the sulphurous dioxide has consisted only in the replacement of the atom of bromine by hydrogen—a replacement observed in other cases by Stenhouse[1] and by Earle and one of us.[2] The conclusion that the black compound is a derivative of paraquinone is confirmed by the observation that it shows none of the tendency to form addition-compounds, which is so characteristic of orthoquinones. We can, therefore, safely consider it the dianilinobromparaquinoneanil,

$$C_6HBr(C_6H_5NH)_2ONC_6H_5.$$

Such conversions of ortho- into paraquinones are not rare—Zincke observed them in the action of aniline on β-naphthoquinone,[3] and on chlor- and dichlor-β-naphthoquinone [4](in fact he did not succeed in isolating the β-anilino compounds); Koch and one of us[5] with the chloroform solution of orthobenzoquinone. Liebermann[6] has given a satisfactory explanation of these conversions, which take place, first by the entrance of an anilino group into the ring in the para position to one of the carbonyl groups; second, the hydrogen from this anilino group is transferred to the second carbonyl group forming an oxyparaquinoneanil; and finally, the further action of aniline replaces the hydroxyl by an anilino group. Andersen[7] has prepared a dianilinochlorparaquinoneanil by the action of aniline on trichlorquinonechlorimide, which melts at 195°, a higher temperature than the melting-point of our brom-compound. It may, however, have a different constitution.

If the dianilinobromparaquinoneanil was heated with aniline and alcohol for four hours it was converted into the dianilinoparaquinoneanil,[8]

[1] Ann. Chem. (Liebig), Supplement, 8, 20 (1872).
[2] This JOURNAL, 26, 46 (1901).
[3] Ber. d. chem. Ges., 14, 1493 (1881); *Ibid.*, 15, 481 (1882).
[4] *Ibid.*, 19, 2498 (1886).
[5] This JOURNAL, 26, 33 (1901).
[6] Ber. d. chem. Ges., 14, 1664 (1881); more fully Liebermann and P. Jacobson: Ann. Chem. (Liebig), 211, 73 (1882).
[7] J. prakt. Chem. [2], 28, 429 (1883).
[8] Zincke and Hagen: Ber. d. chem. Ges., 18, 785 (1885).

$$C_6H_2(C_6H_5NH)_2ONC_6H_5,$$

recognized by its melting-point, 202° to 203°, and crystalline form. It follows from this that dianilinodibromorthoquinone or any of its derivatives will also give this compound under the same conditions. The aniline in this case has acted only by replacing the atom of bromine by hydrogen, probably with the formation of tribromaniline; and the atom of bromine must have been replaced in a similar way in the conversion of the dianilinodibromorthoquinone into dianilinobromparaquinoneanil. This furnishes two new examples of the abnormal replacement of bromine by hydrogen, which has been studied for so many years in this laboratory.

The constitution of the dianilinoparaquinoneanil has been settled without much doubt by the following series of transformations: It is converted into azophenin by long heating with aniline at 180° to 200°; azophenin by long boiling with sulphuric acid and alcohol gives aniline and the 2,5-dianilinoquinone.[1] It follows, therefore, that the dianilinoparaquinoneanil has the structure

$$O1,NC_6H_54,(C_6H_5NH)_22,5.$$

As our brom-compound is converted into this so easily, it must have a similar structure with the bromine at either 3 or 6, and consequently one of the atoms of bromine in dianilinodibromorthoquinone is ortho to one of the carbonyl groups, unless, indeed, in the series of reactions for the conversion of the ortho- into the paraquinone one quinone oxygen has been replaced by hydrogen, which is such a strained hypothesis that it seems unworthy of consideration. As it is highly improbable that the dianilinodibromorthoquinone is unsymmetrical, its structure can be safely accepted as

$$O_21,2.Br3,6.(C_6H_5NH)_24,5,$$

and this is the constitution which would have been expected, because, judging from analogy, the atoms of bromine para to the two atoms of oxygen would be most liable to replacement. Kehrmann[2] has shown that in paraquinones two amino groups

[1] O. Fischer and Hepp: Ber. d. chem. Ges., 21, 2618 (1888).
[2] Ber. d. chem. Ges., 23, 907 (1890).

always enter the molecule in the para position to each other. It would seem from the foregoing considerations that this rule does not apply to orthoquinone.

Some experiments on the reduction of the dianilinodibrom-orthoquinone gave products showing the qualitative tests for pyrocatechin, but owing to lack of time they were not studied thoroughly.

We also include in this paper the description of some work upon the reduction-product from hexabromorthoquinopyrocatechin ether. Koch and one of us[1] found that this substance did not dissolve in sodic hydrate, and there seemed some doubt, therefore, as to whether it really was the expected diatomic phenol. We have now proved that it contains the hydroxyl group, since treatment with benzoyl chloride converted it into a monobenzoic ester,

$$C_6Br_4O_2C_6Br_2OHOCOC_6H_5,$$

a white, crystalline body. We obtained indications that a dibenzoic ester could be obtained by the Baumann-Schotten method, but as the monobenzoic ester had settled the point in question we did not try to isolate the dibenzoic ester.

EXPERIMENTAL PART.

The tetrabromorthobenzoquinone used in this work was prepared by the method of Zincke,[2] that is the oxidation of tetrabrompyrocatechin dissolved in glacial acetic acid, with fuming nitric acid also diluted with glacial acetic acid. The details of this preparation are given in the paper by Koch and one of us.[3] We have to add to what is said there, that it is important to filter off the tetrabromorthoquinone with the least possible delay, as it decomposes rapidly if left in contact with the oxidation solution. The quinone should not be dried at temperatures above 70°, as it decomposes when heated above that point. Our yields were somewhat better than those obtained by Koch and one of us: From 20 grams of pyrocatechin we obtained from 60 to 70 grams of tetrabrompyro-

[1] This JOURNAL, 26, 36 (1901).
[2] Ber. d. chem. Ges., 20, 1777 (1887).
[3] This JOURNAL, 26, 34 (1901).

catechin in place of 59 to 63 grams, and 30 grams of the tetrabrompyrocatechin gave 21 grams of tetrabromorthoquinone, a yield of 70 per cent of the theory instead of the 60 per cent in the earlier work. As before, the tetrabromorthoquinone was used without recrystallization, because this was such a wasteful process owing to the action of almost all solvents on it. The substance used by us melted at 145° to 146° instead of 150° to 151°.

Reduction of the Hexabromorthoquinopyrocatechin Ether, $C_6Br_4O_2C_6Br_2O_2$.

In the previous paper by Koch and one of us[1] this reduction was described, and some account of the product was given. Since, however, it was insoluble in sodic hydrate it did not seem certain that this product contained two hydroxyl groups, as was indicated by the ease with which it passed back to the original (quinone) substance by oxidation. We have therefore taken up again the study of this substance, as upon its nature rests the constitution of the hexabromorthoquinopyrocatechin ether.

The red ether for these experiments was prepared by the method of Koch and one of us, that is to a solution of 11 grams of tetrabromorthoquinone and 10 grams of tetrabrompyrocatechin in 470 cc. of glacial acetic acid 180 cc. of water were added, and the mixture allowed to stand twenty-four hours in a warm place. The red precipitate thus formed was filtered out and washed thoroughly with hot alcohol. In this way 12.5 to 13 grams were obtained, that is about 72 per cent of the theoretical yield. The reduction of the ether was carried on as before.[2] Five grams of the red hexabromorthoquinopyrocatechin ether suspended in water were exposed to the action of sodium amalgam for two or three days in a flask, which was kept filled with carbonic dioxide. The product, which had changed from red to white, was filtered out, and turned to a dull-purple color on exposure to the air. It was washed with dilute acetic acid, water, and alcohol, dried at 100°, and purified by crystallization from hot nitrobenzol.

[1] This JOURNAL, **26**, 38 (1901).
[2] *Ibid.*, **26**, 38 (1901).

The solvent should not be raised to its boiling-point, as this causes a decomposition of the substance. The pure compound, which we found melts at 304° to 307°, was dried at 100°, and analyzed with the following result:

0.2398 gram substance gave 0.1885 gram CO_2 and 0.0133 gram H_2O.

	Calculated for $C_{12}Br_4(OH_2)O_2$.	Found.
C	20.87	21.44
H	0.29	0.62

The properties of the substance agreed with those previously observed except that the crystals from nitrobenzol appeared as iridescent scales instead of short needles. An aqueous solution of sodic hydrate does not dissolve it, as observed in the earlier work, but turns it dark-purple. An alcoholic solution of sodic hydrate seems to decompose it very thoroughly, as oxalic acid was the only product recognized.

Action of Benzoyl Chloride on the Reduction-product.

In order to obtain the object of this work—the testing of the body for hydroxyl groups—we next treated it with benzoyl chloride. One gram of the purplish crystals of the reduced substance was moistened with 2 to 3 cc. of benzoyl chloride and warmed gently till the reaction had started, as shown by effervescence. On cooling, the whole solidified to a pulpy mass of white crystals, which was warmed twice more with fresh portions of benzoyl chloride in order to complete the reaction. The crystals thus obtained were treated with a large amount of hot alcohol, washed with hot alcohol, and recrystallized twice from hot nitrobenzol, after which they were washed with alcohol, dried at 100° and analyzed with the following result:

0.1483 gram substance gave, by the Carius method, 0.2095 gram AgBr.

	Calculated for $C_{12}Br_4O_2(OH)(OCOC_6H_5)$.	Found.
Br	60.45	60.12

There can be no doubt, therefore, that the substance is a monobenzoyl derivative of the reduced substance, which,

therefore, contains hydroxyl groups. The yield was good, as from 1 gram of the original substance 0.6 gram of the benzoic ester, purified by recrystallization, was obtained. Attempts to make the dibenzoyl compound by the Baumann-Schotten method gave mixtures of varying composition.

Properties of the Monobenzoyl Ester of the Hexabromorthodioxypyrocatechin Ether.—It is a white, crystalline substance melting at 316° to 318°. It is essentially insoluble in the common solvents, although very slightly soluble in benzol or acetone; soluble in nitrobenzol, which is the best solvent for it.

Action of Hydrobromic Acid on the Hexabromorthoquinopyrocatechin Ether.

The behavior of the ether with hydrobromic acid was analogous to that with hydrochloric acid, already observed by Koch and one of us.[1] Five-tenths gram of the red ether was heated in a sealed tube to 100°, for twenty-four hours, with 5 to 6 cc. of distilled hydrobromic acid (boiling at 126°). The products were bromine, recognized by its smell, and the formation of a blue color with potassic iodide and starch, a purplish solid looking like the reduction-product with sodium amalgam, not melting below 300°, and converted by nitric acid into the original red ether—properties which identify it as the hexabromorthodioxypyrocatechin ether—and a white, crystalline substance, soluble in hot water and recognized as a substituted pyrocatechin by the green color-test with ferric chloride. The amount of this latter body was not very great, but by oxidizing the reduction-product with nitric acid and heating again with hydrobromic acid more of it was obtained, so that it was evident that a sufficient number of such treatments would convert the ether completely into this substituted pyrocatechin (probably tetrabrompyrocatechin). In this respect the hydrobromic acid reduction was entirely analogous to the reduction with sodium amalgam described by Koch and one of us.

Action of Aniline on Tetrabromorthoquinone.

After a number of experiments we found that the anilino

[1] This JOURNAL, 26, 40 (1901).

derivatives of tetrabromorthoquinone were most conveniently prepared as follows: A solution of 5 grams of tetrabromorthoquinone in 100 cc. of alcohol was added to a cold mixture of 7.5 grams of aniline and 100 cc. of alcohol, in small portions at a time, with vigorous stirring. A light-brown, very bulky precipitate formed at once, which rendered the liquid so pasty by the time half the quinone had been added that it was best to filter out the precipitate with the pump and continue the addition of the rest of the quinone to the filtrate. Upon stirring the mixture of quinone and the filtrate, a yellow body crystallized out in the track of the rod on the sides of the beaker, and the light-brown substance at first mentioned was converted into this same yellow compound if it was allowed to stand in contact with the liquid for half an hour or less. The alcoholic filtrate from the yellow crystals, if allowed to stand over night at ordinary temperatures, or if boiled for a few minutes, deposited lustrous, black crystals of a third compound, but, if the filtrate was boiled for about four hours, it formed reddish-brown crystals of the dianilinoparaquinoneanil. Of the four products obtained from this reaction, the last two are derivatives of parabenzoquinone. The first two are derivatives of dianilinodibromorthobenzoquinone, and it will be well, therefore, to describe this compound before considering its derivatives.

Dianilinodibromorthobenzoquinone, $C_6Br_2(C_6H_5NH)_2O_2$.–This substance was most conveniently made from the pale-brown, voluminous precipitate, which formed the first product of the action of aniline in alcoholic solution on the tetrabromorthoquinone (see the preceding section). This is an addition-compound of the dianilinodibromorthoquinone and aniline. To remove the additional aniline, the precipitate was allowed to dry at ordinary temperatures to get rid of the adhering alcohol, and then heated to about 50° with a mixture of 5 parts of benzol and 1 part of ligroin. After heating for a few minutes, the substance had changed from pale-brown to reddish-purple, the solid was then filtered out and digested in the same way with a fresh quantity of the mixture of benzol and ligroin, and these digestions with fresh portions of the

mixed solvents were repeated three or four times, after which the substance was purified by crystallization from the boiling benzol and ligroin mixture (5 : 1) until it showed the constant melting-point 160°. The first benzol and ligroin filtrates obtained in this process deposited some of the pale-brown addition-compound on standing and contained aniline. The substance melting at 160° was dried at 100° and analyzed with the following results:

I. 0.3216 gram substance gave 17.2 moist N at 16° and 776 mm. pressure.

II. 0.2054 gram substance gave, by the Carius method, 0.1717 gram AgBr.

III. 0.2447 gram substance gave 0.2063 gram AgBr.

	Calculated for $C_6Br_2(C_6H_5NH)_2O_2$.	Found. I.	II.	III.
N	6.25	6.29	....	....
Br	35.71	....	35.57	35.88

Properties of Dianilinodibromorthobenzoquinone.—It crystallizes from benzol in pointed needles of a dark, reddish-purple color. It melts at 160°, and is easily soluble in benzol, glacial acetic acid, or acetone; slightly soluble in alcohol or ether; very slightly soluble in ligroin. The best solvent for it is a boiling mixture of benzol and ligroin. Strong hydrochloric acid has almost no effect upon it. Strong nitric acid dissolves it with decomposition; strong sulphuric acid dissolves it with a yellowish-green color; hot sodic hydrate solution dissolves it with decomposition. Tin and hydrochloric acid, or a solution of sulphurous acid, reduces it easily to a substance giving tests for pyrocatechin. Its most striking property is the ease with which it forms addition-compounds with aniline or alcohols, some of which are described in the following sections.

Addition-compound of Aniline and Dianilinodibromorthoquinone, $C_6Br_2(C_6H_5NH)_2O_2C_6H_5NH_2$.—This substance is the pale-brown precipitate formed at first by the action of aniline on tetrabromorthoquinone in alcoholic solution. For analysis it was purified by two crystallizations from boiling benzol. This method of purification seems strange when it is remem-

bered that the body is decomposed into aniline and dianilinodibromorthoquinone by treatment with benzol and ligroin at 50°. The most probable explanation is that the product is decomposed by solvents in which the dianilinodibromorthoquinone is only slightly soluble, whereas solutions in benzol and similar solvents, in which the quinone is freely soluble, deposit the unaltered addition-compound. For analysis, it was dried *in vacuo*.

I. 0.1970 gram substance gave, on combustion, 0.3868 gram CO_2 and 0.0700 gram H_2O.

II. 0.2502 gram substance gave, by the Carius method, 0.1731 gram AgBr.

	Calculated for $C_6Br_2(C_6H_5NH)_2O_2C_6H_2NH_2$.	Found. I.	Found. II.
C	53.23	53.56	....
H	3.51	3.95	....
Br	29.57	....	29.45

The results of this analysis are confirmed by the following observations: In converting the addition-compound into dianilinodibromorthoquinone by digestion with benzol and ligroin, the filtrates were found to leave a residue of aniline on evaporation. The aniline was recognized by giving a soluble chloride, the isonitrile reaction with chloroform and potassic hydrate, and forming again the addition-compound when treated with tetrabromorthoquinone. The addition-compound is also easily made by boiling the dianilinodibromorthoquinone with the calculated amount of aniline dissolved in benzol.

Properties of $C_6Br_2(C_6H_5NH)_2O_2C_6H_2NH_2$.—It crystallizes from boiling benzol in pale-brown, long, fine needles. It begins to lose aniline if warmed for some time at 50° to 60°, but the product does not seem to be the dianilinodibromorthoquinone, apparently because the aniline acts further upon it at this temperature. If heated rapidly, it melts with decomposition between 121° and 124°. The slight stability of the substance is also shown by its complete decomposition by the action of a solvent-like benzol and ligroin (5 : 1), in which the dianilinodibromorthoquinone is only slightly soluble. It is also decomposed by hot glacial acetic acid, or even by boiling

with water. It is freely soluble in alcohol, benzol, or acetone, although the alcohol solution gradually decomposes in the way described in the next section; slightly soluble in ether or ligroin. Strong hydrochloric acid decomposes and dissolves it (difference from the dianilinodibromorthoquinone); strong nitric acid also dissolves it with decomposition; strong sulphuric acid dissolves it with a yellowish-green color; hot sodic hydrate solution dissolves it with decomposition.

Addition-compound of Dianilinodibromorthobenzoquinone with Ethyl Alcohol, $C_6Br_2(C_6H_5NH)_2O_2C_2H_5OH$.—The yellow precipitate formed during the action of aniline and alcohol on tetrabromorthoquinone was this body. It was also easily obtained by moistening the dianilinodibromorthoquinone or its aniline addition-compound with ethyl alcohol, and allowing the mixture to stand for several days. It was purified by crystallization from warm benzol, care being taken that the temperature did not rise above 50°. After two such recrystallizations it was dried *in vacuo* and analyzed with the following results:

I. 0.3604 gram substance gave 19.2 cc. moist N at 18° and 768 mm. pressure.

II. 0.1644 gram substance gave, by the Carius method, 0.1247 gram AgBr.

III. 0.1717 gram substance gave 0.1294 gram AgBr.

IV. 0.1548 gram substance gave 0.1175 gram AgBr.

V. 0.2167 gram substance gave 0.1647 gram AgBr.

	Calculated for $C_6Br_2(C_6H_5NH)_2O_2C_2H_5OH$.	Found. I.	II.	III.	IV.	V.
N	5.67	6.22	....	....	....	....
Br	32.39	....	32.28	32.08	32.32	32.34

For greater certainty the amount of ethyl alcohol in it was determined by Zeisel's method[1] with the temperature of the baths modified to correspond with ethyl iodide.

0.3124 gram substance gave, by Zeisel's method, 0.1608 gram AgI.

	Calculated for $C_6Br_2(C_6H_5NH)_2O_2C_2H_5OH$.	Found.
OC_2H_5	9.11	9.83

[1] Monatsh. Chem., **6**, 986; **7**, 406; or Sitzber. Akad. Wiss. Wien., **92** [2], 1431; **94** [2], 341.

Properties of $C_6Br_2(C_6H_5NH)_2O_2C_2H_5OH$.—It crystallizes from benzol in bright-yellow plates of about the color of plumbic chromate. These plates are oblong and nearly rectangular, but careful observation shows that the short sides consist of two planes at a reentering angle so obtuse that they might easily be mistaken for a straight line. If heated rapidly, it melts fairly constantly at 142°, but this melting is accompanied by decomposition, as the substance turns black and increases in volume. The melting-point, therefore, is much influenced by the length of the heating, and is the same only when care is taken to make the conditions the same. The substance decomposes by long heating at temperatures far below its melting-point, and this decomposition was studied as follows: About 0.3 gram of the body, carefully dried in a current of air and *in vacuo*, was heated in a small test-tube provided with a narrow air-condenser dipping under a few drops of water. After heating to 110° to 125° for nearly three hours, drops of a colorless liquid were observed in the condenser. These were washed out with very little water and tested with iodine and potassic hydrate for ethyl alcohol. The presence of iodoform was established by the yellow color and the odor, so there can be no doubt that alcohol had distilled off. The solid residue in the test-tube was blackened and partially fused, and after one crystallization from the mixture of benzol and ligroin (5 : 1) melted at a higher temperature (150° to 160°) than the original substance. We did not attempt to isolate the dianilinodibromorthoquinone from it.

In a second experiment, the temperature was kept at 90° to 95°, and the substance heated in a watch-glass to determine the amount of alcohol given off. The weighings were taken at intervals of two or three hours, and showed a fairly rapid loss for the first twenty-three hours, when it amounted to 9.8 per cent. If $C_6Br_2(C_6H_5NH)_2O_2C_2H_5OH$ loses the 1 molecule of ethyl alcohol, the loss would be 9.31 per cent. After the twenty-third hour, the amount of loss in three hours diminished to a very marked extent, but continued heating caused a slight additional loss up to forty-eight hours, when the experiment was stopped. It seems, therefore, that the

alcohol is given off fairly rapidly and completely even at this low temperature, and that this escape of the alcohol is accompanied by a gradual decomposition of the residual quinone. A loss of alcohol from this substance was observed even at 60°.

The substance dissolves very freely in acetone; it is moderately soluble in alcohol, ether, or benzol; very slightly soluble in ligroin. Hot glacial acetic acid dissolves it with decomposition, shown by the dark-purple color of the solution, and it is also decomposed by continued boiling of its solutions, as would be expected when the slight stability of the substance toward heat is remembered. A boiling mixture of benzol and ligroin (5 : 1) is especially well adapted to bring about this change. Strong hydrochloric acid dissolves it, and aqueous sodic hydrate, when hot, has the same effect.

Addition-compound of Dianilinodibromorthobenzoquinone and Methyl Alcohol, $C_6Br_2(C_6H_5NH)_2O_2CH_3OH$.—This substance was made by the action of aniline on tetrabromorthoquinone dissolved in methyl alcohol. This method of preparing it is better than moistening the dianilinodibromorthoquinone with methyl alcohol, as in that case the product dissolves in the methyl alcohol.

0.2902 gram substance gave, by the Carius method, 0.2269 gram AgBr.

	Calculated for $C_6Br_2(C_6H_5NH)_2O_2CH_3OH$.	Found.
Br	33.33	33.28

It resembles the corresponding ethyl compound in most respects, but has a somewhat lighter yellow color, and melts with decomposition at 144° to 145°, that is a few degrees higher than the ethyl alcohol addition-product.

Dianilinobromparaquinoneanil, $C_6HBr(C_6H_5NH)_2ONC_6H_5$.—This is the product most easily obtained by the action of aniline on tetrabromorthoquinone, as it is stable enough to require in its preparation no particularly careful attention to detail, such as is necessary in making the orthoquinone compounds just described, and, further, all these orthoquinone derivatives are converted easily into this dianilinobromparaquinoneanil.

It was most easily prepared by the method given under the heading, Action of Aniline on Tetrabromorthoquinone, that is by allowing the alcoholic filtrate from the aniline addition-compound of dianilinodibromorthoquinone to stand for several hours, or more quickly by boiling it for a few minutes. Other methods of preparation were: Boiling dianilinodibromorthoquinone or its addition-compounds with alcohol and a little aniline for a short time. Adding aniline to a cold benzol solution of tetrabromorthoquinone, when a precipitate was formed consisting of the aniline addition-compound of dianilinodibromorthoquinone and aniline chloride. On boiling this precipitate with a mixture of alcohol and benzol it was converted into the dianilinobromparaquinoneanil. Finally, by adding aniline to a boiling solution of tetrabromorthoquinone in alcohol or in glacial acetic acid. It was purified by recrystallization from a boiling mixture of equal parts of benzol and methyl alcohol until it showed the constant melting-point 173°, when it was analyzed with the following results:

I. 0.1198 gram substance gave, on combustion, 0.2875 gram CO_2 and 0.0509 gram H_2O.

II. 0.3685 gram substance gave 31.5 cc. moist N at 26°.5 and 772 mm. pressure.

III. 0.2422 gram substance gave, by the Carius method, 0.1027 gram AgBr.

	Calculated for $C_6HBr(C_6H_5NH)_2ONC_6H_5$.	Found. I.	II.	III.
C	64.86	65.45	....	....
H	4.05	4.72	....	....
N	9.46	....	9.59	....
Br	18.02	....	....	18.04

The molecular weight was also determined by the freezing-point method in benzol.

I. 0.2811 gram substance, in 20 grams benzol, produced a depression $\Delta = 0°.185$.

II. 0.1245 gram substance produced a depression $\Delta = 0°.073$.

	Calculated for $C_6HBr(C_6H_5NH)_2ONC_6H_5$.	Found. I.	II.
Mol. wt.	444	372	418

These results leave no doubt as to the formula of the compound. Our reason for assigning it to the para rather than the ortho series is that an ethereal solution of sulphurous dioxide in the cold converts it into the known dianilinoparaquinoneanil, and it seems improbable that a passage from the ortho to the para group could take place under such conditions. This conclusion is supported by the fact that it does not show the strong tendency to form addition-products, which is so characteristic of the orthobenzoquinone derivatives. The mechanism of the change from the ortho to the para compound is discussed in the introduction to this paper.

Properties of Dianilinobromparaquinoneanil.—It crystallizes from a mixture of benzol and alcohol in jet-black plates with an uncommonly brilliant luster. Thin plates, under the microscope, have a dark yellowish-brown color, which becomes black when the plate is of ordinary thickness. The plates are shaped like spear-heads, that is they have a sharp, rhombic form with a slight reentering angle on each side. Its melting-point was found to be 173°. It is freely soluble in benzol, glacial acetic acid or acetone; moderately soluble in ethyl or methyl alcohol or in ether; it is decomposed by recrystallization from alcohol; very slightly soluble in ligroin. The best solvent for it is a mixture of equal parts of benzol and methyl alcohol. Hot, strong hydrochloric acid dissolves it slowly with a greenish color; strong nitric acid dissolves it with decomposition; strong sulphuric acid dissolves it with a dark purplish-red color, which distinguishes it from the ortho compounds described earlier in this paper, as these impart a greenish-yellow color to strong sulphuric acid. Sodic hydrate has no apparent effect on it, hot or cold. Ether saturated with sulphurous dioxide decolorizes it and deposits crystals of dianilinoparaquinoneanil. The same change is brought about by boiling it for some time with aniline or chloride of aniline and alcohol, and probably more slowly by boiling with alcohol alone. A sample moistened with methyl alcohol, after standing for several weeks, had the melting-point of the original substance, showing that it does not form addition-compounds.

Formation of Dianilinoparaquinoneanil, $C_6H_2(C_6H_5NH)_2ONC_6H_5$.—As has been already stated, this substance, discovered by Zincke and Hagen[1] in 1885, was the final product of the action of aniline on tetrabromorthoquinone in alcoholic solution. We have obtained it in the course of our work in the following ways: Boiling for four hours, the alcoholic filtrates from the preparation of the aniline addition-compound of dianilinodibromorthoquinone; boiling any of the orthoquinone derivatives described in this paper with alcohol and aniline for several hours; boiling the dianilino-bromparaquinoneanil with aniline and alcohol for several hours; or treating it in the cold with a saturated ethereal solution of sulphurous dioxide.

The identification of this substance gave us a great deal of trouble. The pure substance melts, according to Zincke and Hagen, at 202° to 203°, but after many recrystallizations from a mixture of equal parts of benzol and alcohol we could not raise the melting-point of our preparations above 199°. Finally, however, by repeated crystallization from methyl alcohol, we succeeded in eliminating the impurity and raising the melting-point to 202° to 203°. To establish the identity of our substance beyond doubt it was compared with some dianilinoparaquinoneanil made from paraquinone by the method of Zincke and Hagen. This, like our specimen from the tetrabromorthoquinone, melted obstinately at about 199°, and could be raised to its true melting-point only with great difficulty. On comparing the two specimens, the only difference observed was a slight one in color, our specimen was purple, that made by Zincke and Hagen's method dark-brown. The crystalline habit of the two was exactly alike. From a mixture of benzol and alcohol both deposited, at first, two slender needles, crossing almost, but not quite, at a right angle. These two needles then became crossed by a large number of shorter needles, apparently at right angles to the main needle, and lying as close together as the teeth of a comb—a very characteristic form. From alcohol alone both gave bunches or sheaves of very long, fine needles. There can be no doubt,

[1] Ber. d. chem. Ges., 18, 787 (1885).

therefore, that our substance is the dianilinoparaquinoneanil. We may add that it formed no addition-compound with methyl alcohol even after standing with it for several weeks.

Reduction of Dianilinodibromorthoquinone.

Our experiments in this direction were left in an unfinished state because of the pressure of other more important work. We think it best, however, to give a brief statement of the results obtained, and hope that this branch of the work will be continued in this laboratory in the near future.

Tin and hydrochloric acid reduced the ethyl alcohol addition-compound of the dianilinodibromorthoquinone to a white body, which we did not succeed in purifying, but which gave tests for a pyrocatechin with plumbic acetate and ferric chloride.

Sulphurous dioxide reduces tetrabromorthoquinone to tetrabrompyrocatechin, either in aqueous or ethereal solution, apparently quantitatively. With dianilinodibromorthoquinone, the aqueous solution of sulphurous dioxide turned yellow, and left, on evaporation, a partially crystalline residue, which gave a test for a pyrocatechin with ferric chloride, but the yield was exceedingly small, as the greater part of the quinone was left unaltered.

Sulphurous dioxide in ethereal solution yielded more promising results. A saturated solution of dianilinodibromorthoquinone in anhydrous ether (dried over sodium) was saturated with sulphurous dioxide, when, on standing, rosettes of dark-green needles separated on the walls of the vessel. As it was too unstable to admit of recrystallization, the crystals were purified by washing with ether. Upon repeating this experiment we did not succeed in obtaining this green substance again, and have not yet been able to give the time necessary to discover the proper conditions for preparing it with certainty. It forms rosettes of small, green needles, which melt at 186° to 188°. It is decidedly unstable, as, when heated, it turns dark-red, and solution in alcohol produces the same change of color. The green color, the instability, and the easy conversion into a red body all point to its

being formed by the reduction of part of the quinone to a pyrocatechin, which then combines with some of the unreduced quinone to form a substance analogous to quinhydrone. The substance dried *in vacuo* gave the following result on analysis:

0.1644 gram substance gave, by the Carius method, 0.0834 gram AgBr.

	Calculated for $C_6HBr(C_6H_5NH)_2O_2C_6HBr(C_6H_5NH)_2(OH)_2$.	Found.
Br	21.62	21.59

$C_6HBr(C_6H_5NH)_2O_2$ contains 21.68 per cent of bromine.

Our results are obviously insufficient to establish the nature of this substance with certainty, which must be left to future experiments.

If common (undried) ether was used, a different result was obtained. A saturated solution of dianilinodibromorthoquinone in commercial ether was saturated with sulphurous dioxide and allowed to stand at ordinary temperatures. After twelve hours it had deposited a considerable amount of a white body in long, fine needles, and about one-tenth as much of dark-colored crystals, in which three different forms were recognized—large, amber-colored needles in feather-like aggregations; minute, dark-colored, hexagonal plates; and blunt, rounded needles crossing at an angle of about 60°. These three substances were present in such small quantities that only a qualitative study could be made of them. They dissolved easily in alcohol, and the solution gave a heavy, white precipitate with plumbic acetate, which was soluble in acetic acid. They also gave a deep-green color with ferric chloride. From these observations we infer that one or more are substituted pyrocatechins. The amber-colored needles melted (impure) from 160° to 163°.

The white substance, which was the principal product of the reaction, was roughly separated from the dark crystals by decantation, and crystallized from a mixture of alcohol and ether (1 : 3). It formed long, white needles and was decidedly stable for a substance of this group. It did not melt below 300° and was slightly soluble in cold water, more easily

in hot; very freely soluble in methyl or ethyl alcohol; almost insoluble in ether or benzol. Its aqueous solution gave a precipitate with argentic nitrate, and the substance could be salted out of its aqueous solution with salt or hydrochloric acid. Very dilute sodic hydrate dissolved it, giving a clear, greenish solution; cold, strong sodic hydrate seemed to have no action on it, but when hot decomposed it. All these properties indicate that it is a bromide. Its alcoholic solution gives a slight precipitate with plumbic acetate, and ferric chloride imparts a slight green color to it, so that it may be a pyrocatechin. Unfortunately, we did not succeed in purifying it thoroughly for analysis, three different samples giving the following percentages of bromine, 35.11, 37.01, 37.81, so that we can make no definite statement about its composition. It seems possible, however, that it is a pyrocatechin ether derivative, as $C_6Br_3(C_6H_5NH)_2O_2C_6(C_6H_5NH)_2(OH)_2HBr$ contains 35.56 per cent of bromine; but, on the other hand, it is hard to bring the formation of such an ether into harmony with the most probable structure for the dianilinodibromorthoquinone, $O_1,1,2.(C_6H_5NH)_2,4,5.Br_3,6$. The more thorough study of this interesting substance will be taken up in this laboratory in the near future.

Attempts to prepare analogous pyrocatechin ethers from pyrocatechin or tetrabrompyrocatechin by the action of sulphurous dioxide in ethereal solution led to no result.

The hexabromorthoquinopyrocatechin ether, when treated with aniline, gave the same products as the tetrabromorthoquinone.

A BUNSEN MEMORIAL.

A movement is on foot to erect a suitable memorial in honor of Robert Bunsen in Heidelberg, where he lived and labored for nearly half a century. The arrangements are in charge of Professor Curtius, who is aided by a large committee of prominent chemists in Europe and America. This country is represented by Professors Jackson, Michael, and Nef.

It is hoped that all former students and friends of Bunsen will show their interest in the work by subscribing to the fund which is being raised. Professor C. Loring Jackson, Cambridge, Mass., has consented to act as treasurer for the American fund, and all subscriptions should be sent to him.

REVIEWS.

CHEMICAL EXERCISES FOR CLASSROOM AND HOME STUDY. By RUFUS P. WILLIAMS, Teacher of Chemistry in the English High School, Boston, and Author of Elements of Chemistry, Chemical Experiments, etc. Boston: Ginn & Co. 1903.

These exercises are printed as headings on a letter-pad. The space below and on the reverse of the leaf is to be filled by the student. The leaves are detachable. There are 100 exercises covering inorganic chemistry as commonly taught in the first year of a college course. The questions are admirably chosen, and the result of the use of the exercises must be beneficial. E. R.

A TEXT-BOOK OF QUANTITATIVE CHEMICAL ANALYSIS. By FRANK JULIAN. Illustrated. First Edition. St. Paul, Minn.: The Ramsay Publishing Co. pp. 604.

Of the five parts into which the subject matter of this volume is divided, the first deals with the general principles which underlie the methods of quantitative analysis, and the operations which are common to all analyses. It is divided into nine chapters, including those upon methods of sampling, the purchase and care of balances and weights, the processes of solution, evaporation, precipitation, filtration, and the like, the principles of volumetric and gas analysis, "attributive methods," and calculation of analyses, and a discussion of errors and precautions.

Part 2 comprises a detailed description of twenty-four practice exercises in analysis, including such substances as alcohol, coffee, standard acid and alkali, vinegar, chloral hydrate, hydrastis, standard permanganate, forge scale, chrome yellow, metol, galena, lard, air, and wollastonite.

Part 3 is devoted to special methods and technical analysis, the former including the processes of colorimetry, fire assay, electrolysis, ultimate and proximate organic analysis, and chlorimetry, which are applied, among other instances, to irons and steels, iron ores, coal, natural waters, fertilizers, the alcohols and alkaloids, tannins, carbohydrates, oils, fats, soaps, milk, butter, urine, and the organic dyestuffs.

Part 4 contains more "notes and observations relating to the principles and practice of the art in general that may be of interest to the student," and an appendix presents a still further discussion of "certain phases of the important subject of the practice of technical and industrial chemical analysis." The appendix also contains tables and an index.

The author, in his preface, states that the volume is intended to aid students who can devote but a limited time to the study of quantitative analysis, and that he deems it wise to present a "general view of the art as practised at this time," for which purpose he avoids minutely detailed directions, as far as possible, giving greater prominence to underlying principles, in order that the student may, thereby, obtain a broader view and "a more comprehensive knowledge of the art than is afforded by the study of a string of detailed recipes, however practically useful they may be." The volume is also intended as an "introduction to monographs on special departments of technical analysis."

In pursuance of the purpose thus outlined, the author has brought together a mass of material which has involved much careful thought and compilation, and contains a great deal of useful suggestion and sound advice, which cannot fail to be of great value to the student (or the general reader) provided he has the patience and perseverance to ferret it out of the 600 or more pages of inexcusably fine print. That the idea of laying stress upon principles of general application as well as upon the details and the technique of manipulation is sound, no good teacher of analytical chemistry will question. It would seem, however, that in this text-book the author has enunciated general principles at such great length, and has substituted general statements for vital details to such an extent, that the book falls short of furnishing effective aid to either student or practising analyst; because, in a large number of instances no references are given which enable the reader to turn to original sources of information regarding the processes mentioned. So far as such references are given, however, assuming that a chemical library is at the command of the reader, this volume may be found useful, in that it furnishes a general discussion of the methods in use for a particular purpose.

The author's pen moves freely and he has allowed himself almost unlimited space in the expression of his ideas. As a result there is considerable repetition (especially of material in Parts 1, 4, and the appendix) and the force of many statements is likely to be lost upon the student because of their

lengthy presentation. It is hardly conceivable that the beginner will be able to assimilate the directions and advice included in 201 pages of fine print, and he will find it difficult to sift out of these pages the vital points.

The intermingling of proximate and ultimate methods of analysis in the exercises for practice, a part of which are enumerated above, is unusual and seems to present difficulties of manipulation and of interpretation of results, which would be confusing to the beginner even though he is asked to make a "determination of the atomic weight of chlorine" as his third exercise. The weighing of ammonium sulphate (p. 221) as a representative method for the standardization of a sulphuric acid solution does not appear to be a fortunate choice, and the use of phenolphthalein as an indicator without making any provision for the presence of carbonate in the caustic soda (p. 223) is inaccurate. The statement (p. 192) that weighing to the nearest milligram is, in general, sufficiently exact will hardly hold true in practice where the analyst is often compelled to work with a small weight of material, and the qualifying statement will hardly safeguard the student from gaining an erroneous impression. The statement (p. 103) that crucibles need not be cooled in a desiccator after ignition, if weighed as soon as cool, seems to take no account of the condensation of moisture on the surface of the crucible itself, and that this may vary in amount from hour to hour.

It is, perhaps, a minor criticism that the use of such words as "succussion" for bumping, "encysted" for enclosed, "extrinsic" for outside, and "plications" for folds, seems cumbrous in a scientific treatise for beginners. The substitution of "preventative" (p. 193) for preventive is, doubtless, an accident of proof-reading, to which may also be attributed the large number of badly printed symbols throughout the volume.

The volume contains a great deal that is of interest and value to analysts, and, while its success as a text-book for beginners, if used alone, may be somewhat problematical, it may well serve a useful purpose for teachers and practising analysts as a reference book in conjunction with other works.

H. P. T.

HANDBOOK OF TECHNICAL GAS-ANALYSIS. By CLEMENS WINKLER, PH.D., Professor of Chemistry at the Freiberg Mining Academy. Second English Edition. Translated from the Third German Edition, with some Additions, by GEORGE LUNGE, PH.D., Professor of Technical Chemistry in the Federal Polytechnic School, Zurich. London: Gurney & Jackson. 1902. pp. 190.

The present translation of Winkler's Technical Gas-Analy-

sis appears as an important and opportune contribution to the literature of gas-analysis. Professor Lunge states in his preface that although the book is published as the second English edition, it really represents the third German edition of Winkler's work. The general arrangement of the book is the same as in the preceding edition, from which it differs mainly by presenting a more thorough and detailed discussion of known reactions in the light of recent literature, rather than by material additions of new methods. A chapter is devoted to the collection and preservation of gas samples. In the second and third chapters are considered the commonly used methods of gas-measurement, the determination of the specific gravities of gases, and the various rapid methods of analysis devised by Winkler, Hempel, and Lunge. Special methods are discussed for the determination of carbon dioxide in air, the determination of fire-damp in the air of mines, and for the examination of gases resulting in various chemical manufacturing operations. Some useful tables follow. The solubility of gases in water and other liquids over which they are measured has always presented a serious obstacle to the satisfactory utilization of many reactions which are noted for their sharpness and adaptability to gasometric methods. Although in an indirect manner and without special reference to this always present difficulty, Winkler offers many useful suggestions for overcoming errors incidental to gasometric work, and presents a brief but excellent treatise. Chemists will find this a valuable book. F. C. P.

PRINCIPLES OF DYEING. By G. S. FRAPS, PH.D., Sometime Fellow, Johns Hopkins University, Assistant Professor of Chemistry, North Carolina College of Agriculture and Mechanic Arts. pp. xii + 270, with 22 illustrations in the text. New York: The Macmillan Company. 1903. Price, $1.60.

The author states in the preface that "this book is the result of two years' instruction in dyeing in the classroom and in the laboratory. It aims to be a systematic presentation of the principles underlying the art of dyeing and emphasized by laboratory exercises. It attempts to apply to the teaching of dyeing the same methods of classroom work, which have proved so successful in the teaching of inorganic chemistry and other branches of the science."

The plan of study, which is followed, is to take two members of the first group of dyes and study these with special reference to their action toward the different fibers. Members of the second group of dyes are then taken up, and so on till all the groups have been considered.

A clear idea of the relations between the groups of dyes, their general properties, and their behavior towards different fibers having been gained in this way, the study of the groups of textile fibers is then taken up.

Following this comes the consideration of the machinery for dyeing and bleaching, and the methods of preparing the fibers or fabrics for the dyeing proper. Finally, the different groups of dyes are studied with the principles involved in their application to the different classes of material.

The book contains seventy-nine experiments to be performed by the student in the laboratory, these experiments being, so far as practicable, the processes used in dye-house work.

It is particularly unfortunate that the theories of dyeing given by the author on pages 51 and 52, are stated so briefly and also incorrectly. This part of the book should certainly be rewritten.

The book is well printed and bound and is provided with an excellent index. It can be most heartily recommended as a text-book to those desiring to teach or study the principles of dyeing. W. R. O.

INTRODUCTION TO THE RARER ELEMENTS. By PHILIP E. BROWNING, PH.D., Assistant Professor of Chemistry, Kent Chemical Laboratory, Yale University. New York: John Wiley & Sons; London: Chapman & Hall, Limited. 1903. 8vo. pp. viii + 157. Cloth, $1.50, net.

According to the preface, "This small volume, prepared from material used by the author in a short lecture-course given at Yale University, is intended to serve as a convenient handbook in the introductory study of the rarer elements; that is, of those elements which are not always taken up in a general cause in chemistry."

Advanced students ought certainly to pay more attention to these "rarer elements" than they commonly do, and this book will help them. The time required for a course like that laid out would be well spent. The book is clearly written and the directions for laboratory work are to the point.

The chapter devoted to gold is especially interesting. It is stated here that "As far back as 3600 B. C. in the Egyptian code of Menes, a ratio of value between gold and silver (2.5 : 1) is mentioned." Apparently they did more for silver in those days than the silver-tongued orator of the Chicago convention has since then hoped for and insisted upon.

The last chapter of the book treats of the newly discovered gases of the atmosphere and "recent unconfirmed discoveries." Even victorium, polonium, radium, and carolinium find mention here. I. R.